DEVELOPMENT OF A NEW SYNTHETIC POLYMERISATION TECHNIQUE FOR THE FABRICATION OF SPECIALITY BLOCK COPOLYMERS

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MSc THESIS SUMMARY:

Development of a new synthetic polymerisation technique for the fabrication of speciality block copolymers

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Block copolymers have many applications in a wide range of industries. In medicinal research, the production of amphiphilic block copolymers has gained a lot of interest, for drug delivery and tissue engineering. The current methods used for the block copolymer synthesis are controlled radical polymerisation such as RAFT, ATRP and NMP. These methods have many drawbacks such as a limited selection of monomers for ATRP, specific reaction conditions for NMP and expensive purchasing costs for RAFT agents. Recently, there has been a surge in research to identify alternatives to these techniques. The addition of alkyl halides to radical polymerisation is one alternative which has gained some attention. In the literature, brominated haloalkanes have been used as transfer agents, but the use of bromoform has not been studied extensively. Articles suggested polymers produced using bromoform lead to labile end groups which can undergo further polymerisation. This project focuses on understanding the role of bromoform in radical polymerisation and producing block copolymers using this method.

The results from bromoform-mediated polymerisation showed polymers produced using this technique offered some control for the molar mass for the polymerisation of styrene and MMA. Generally, low disparity polymers were produced when compared to those produced by the conventional radical polymerisation. Using high concentrations of bromoform resulted in low molar mass polymers being obtained ($Đ$ < 1.5) . The results from thermal polymerisation of MMA showed bromoform can behave as a thermal initiator at temperatures above 60 °C. Temperatures below 60 °C resulted in low conversions, and high molar mass polymer being achieved. The activation energy for the thermal polymerisation of MMA using 1 molar equivalents bromoform as a thermal initiator in THF was calculated using an Arrhenius plot, E_a = 95.1 kJ/mol.

Following this, attempts were made to produce PMMA-PS block copolymers using the homopolymers produced from the bromoform-mediated polymerisation. It was discovered the order of homopolymer used as macro-CTA/macro-initiator plays an important role in the formation of the block copolymer. The results showed copolymers can be produced using PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macroinitiator for the polymerisation of styrene monomer in THF. The target ratio of MMA to styrene units for the copolymer was 1:1 in the initial study. The kinetic studies showed a linear progression in molar mass and monomer conversion. GPC data showed the final polymer had an M_n = 54,000 g/mol, and a broad, but unimodal distribution dispersity ($Đ$ = 2.41). The actual ratio from ^{1}H NMR was found to be equal to 1:3.4. Following this, further experiments were conducted with different degree of polymerisations

The research conducted on the polymerisation of styrene and MMA under non-aqueous system has been largely successful. The addition of bromoform to a radical polymerisation has a few advantages: The purchasing price of bromoform is relatively cheap compared to other CTAs and its solubility in water, which could allow reactions to be conducted under aqueous media. For a better understanding of the role bromoform plays in polymerisation reactions, characterisation techniques such as MALDI-TOF should be used to identify the functionality of the polymer end groups.

Key words: Block copolymers, RAFT, ATRP, NMP, CTA, bromoform-mediated polymerisation, macro-initiator, macro-CTA, PMMA, PS, PMMA-*b*-PS, MALDI-TOF.

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ABBREVIATIONS

^{1}H NMR	Proton Nuclear Magnetic Resonance Spectroscopy
ACPA	4,4′-Azobis(4-cyanopentanoic Acid)
AIBN	2,2’-Azobis(isobutyronitrile)
ATRP	Atom Transfer Radical Polymerisation
BCP	Block Copolymer
CRP	Control Radical Polymerisation
CTA	Chain Transfer Agent
Đ	Dispersity
DOSY	Differential Order Spectroscopy
DP	Degree of Polymerisation
FTIR	Fourier Transformer Infrared
GPC	Gel Permeation Chromatography
macro-CTA	Macro Chain Transfer Agent
MMA	Methyl Methacrylate
M_n	Number Average Molecular Weight
M_w	Weight Average Molecular Weight
NMP	Nitroxide Mediated Polymerisation
NMR	Nuclear Magnetic Resonance
PMMA	Poly (methyl methacrylate)
PS	Polystyrene
RAFT	Radical Addition Fragmentation Transfer
T_g	Glass Transition Temperature
TGA	Thermogravimetric Analyzer
UV	Ultraviolet

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CHAPTER 1

INTRODUCTION

1.1. INTRODUCTION TO THESIS

The main goal of this research project is to develop a new synthetic polymerisation technique for the production of speciality block copolymers. The current synthetic techniques used to produce block copolymers are expensive and not suitable for all monomers. In 2014, Thananukul *et.al*[1] suggested block copolymers can be produced using polymers produced using bromoform. The article suggested bromoform acts as a chain transfer agent (CTA). In 1958, Miller[2] suggested bromoform acts as a photo-initiator due to the polarisabilty of the C-Br bond present. Both articles suggested copolymers could be produced due to the presence of labile end groups on the polymer backbone. But both authors have suggested different roles for bromoform. This project aims to identify the role of bromoform in a polymerisation reaction using kinetic studies and produce a variety of block copolymers under non-aqueous systems.

1.2. INTRODUCTION TO POLYMER CHEMISTRY

Polymers are substances composed of large molecules which consist of many smaller structural units called monomers which are covalently bonded together in any conceivable pattern.[3] The mean number of repeat units per chain is termed the number-average degree of polymerisation (DP). If a polymer is composed of one monomer (all the repeat units are identical) it is called a homopolymer. A polymer containing two or more monomers is known as a copolymer. The order and sequence of such monomers determines whether linear copolymers have statistical, alternating or block copolymer architectures (Figure 1.1).[4]

HOMOPOLYMER	A-A-A-A-A-A-A-A-A-A
STATISTICAL COPOLYMER	A-B-A-B-A-A-B-B-A-A
ALTERNATING COPOLYMER	A-B-A-B-A-B-A-B-A-B
AB DIBLOCK COPOLYMER	A-A-A-A-A-B-B-B-B-B
ABA TRIBLOCK COPOLYMER	A-A-A-A-A-B-B-B-B-B-A-A-A-A-A
ABC TRIBLOCK COPOLYMER	A-A-A-A-A-B-B-B-B-B-C-C-C-C-C

Figure 1.1. Schematic diagram for a range of copolymers where the letters (*A*), (*B*) and (*C*) represent monomer units.

Today, both natural polymers, such as starch and cellulose,[5] and synthetic polymers, such as coatings [6] and plastics,[7] are involved in the comfort and facilitation of human life. In industry block copolymers are used as elastomers, dispersants,[8] emulsifiers,[9] and adhesives.[10]

In a given sample, the length of the polymer chains is not all exactly the same chain length. The number-average molecular weight (M_n) is the statistical average molecular weight of all the polymer chains in the sample, *i.e.* the total mass of all the polymer chains divided by the total number of chains.[11] Polymer scientists have used a variety of techniques, such as; viscometry measurements,[12] gel permeation chromatography (GPC),[13] and a variety of nuclear magenetic resonance (NMR) techniques[14] to identify this average.

The weight-average molecular weight (M_w) takes into consideration the molecular weight of each polymer chain in the molecular weight average.[15] Techniques for M_w require more sensitive techniques for determination of molecular size, such as light scattering techniques and GPC.[15] If both M_n and M_w values have been determined the dispersity ($Đ$) can be calculated. The dispersity is a measure of the distribution of molecular mass in a given polymer sample. When a polymer has a dispersity value close to one it can be said to have a narrow molecular weight distribution. M_n, M_w and the $Đ$ can be calculated using Equations 1.1-1.3 below where W_x and w_x define the weight and the weight fraction of molecules with molecular weight M_x, respectively, and the number of moles is given by N_x.[17]

Number average molecular weight, $M_n = \frac{w_x}{\sum N_x} = \frac{\sum N_x M_x}{\sum N_x}$ (Equation 1.1)

Weight average molecular weight, $M_w = \sum w_x M_x = \frac{\sum W_x M_x}{\sum W_x}$ (Equation 1.2)

Dispersity, $Đ = \frac{M_w}{M_n}$ (Equation 1.3)

In an ideal polymerisation reaction, the molecular weight of every single polymer chain would be identical, giving a $Đ$ value of unity. However, perfect control cannot be achieved in current laboratory practice. For current polymerisation techniques used in industry, broad molecular weight distributions (MWDs) are characterised by $Đ > 1.5$ and narrow MWDs are characterised by $Đ < 1.5$.[4]

1.2.1. Step and chain polymerisation

The synthesis of polymers can be achieved by a variety of methods. The methods can be one of two classes, step or chain polymerisation. Step polymerisation was first discovered by Carothers in the 1930s.[18] Carothers synthesised a variety of polyesters following a 'condensation polymerisation' as water was eliminated. Following this, it was discovered a step growth polymerisation proceeds by the combination of two polyfunctional monomers. The polymerisation often occurs with a loss of a small by-product.[19]

In industry, step polymerisation is used to synthesis polyesters, polyamides and polyurethanes.[20] One of the most explored synthetic polymers using this technique is Nylon 6,6. Nylon 6,6 is used as fibres for textiles due to its high mechanical strength, ridgity and good stability under heat and chemical resistance.[21] Nylon 6,6 is made from two monomers each of which contain 6 carbon atoms. Nylon 6,6 can be synthesised in a polycondensation reaction between hexanedioic acid and 1,6-diaminohexane.[22] When these two components polymerise, the amine and acid group combine with loss of a water molecule. Nylon 6,6 can also be synthesised using apidoyl chloride [23] and hexamethylene diamine,[24] in this case HCl is eliminated instead of water. In polyurethane and epoxy polymerisation no by-products are eliminated. Naturally occurring step polymerisation also exist, such as the production of cellulose which is a chain of glucose and polypeptide chains of proteins, which are chains of amino acids.

Characteristics of a step polymerisation include slow increase of molecular weight; large chains are only dominant when high monomer conversion is achieved. Chain polymerisation consists of addition reactions with no elimination of by-products. Typically, there is only one active site per polymer chain, which is passed down the chain as a new monomer unit is introduced. This means that high molar mass polymers are achieved at low monomer conversion.[25] Figure 1.2 shows the difference between the two classes of polymerisation as well as controlled living polymerisation.

Chain polymerisation is discussed further in Section 1.2.2 and controlled polymerisation in Section 1.2.8.

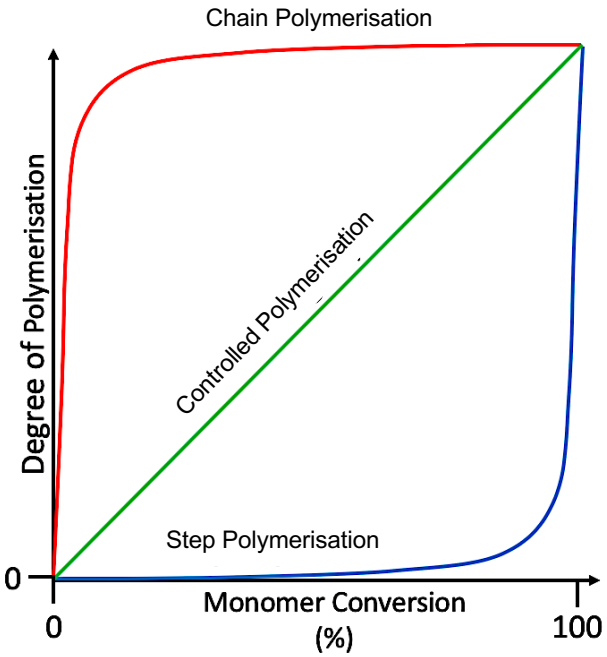


Figure 1.2. Degree of polymerisation *versus* monomer conversion for chain, step and controlled polymerisation.

1.2.2. Radical polymerisation

Radical polymerisation is a chain polymerisation which is widely used for the synthesis of polymers on an industrial scale.[26] The technique is viable for a wide range of monomers such as styrenes, acrylates and amides using both protic and aprotic solvents.[27] The polymerisation technique can be conducted under a range of physical conditions such as bulk, solution, dispersion, suspension or emulsion.[28–30] Radical polymerisation consists of three fundamental steps. These are *initiation*, which involves the formation of radicals followed by the radical's reaction with a vinyl monomer; *propagation*, which is the rapid and progressive addition of monomers to the growing polymer chain without a change to the active centre; and *termination*, which is the destruction of the growing active centre, usually by *combination* (coupling of the radicals of two growing polymer chains) or by *disproportionation*. These three steps have been outlined in Figure 1.3. In addition to these three processes, chain transfer might occur, which is the transfer of the growing active site from the active chain to an inactive one.

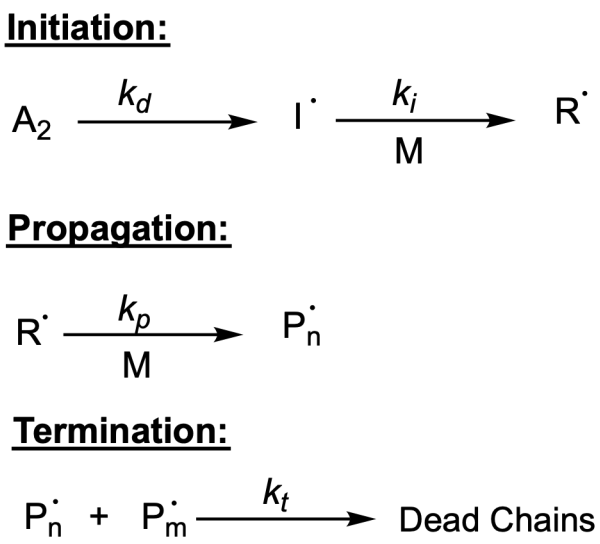


Figure 1.3. Reaction scheme for radical polymerisation.

Initiation involves the generation of radicals by homolytic scission. The radicals can be produced via thermolysis, photolysis, or redox reaction of peroxides, hydroperoxides, azo or diazo compounds.[31] An initiator is typically added to the formulation to act as a radical source.

The two most common thermal initiators used are benzoyl peroxide (BPO) and 2,2'-azo-bis-isobutyrylnitrile (AIBN). Both molecules have a strong tendency to fall apart into two fragments with unpaired electrons. 4,4′-Azo-bis(4-cyanopentanoic acid) (ACPA) is a photochemical initiator which decomposes by irradiation from UV light which has been used

in the literature. Figure 1.4 outlines the thermal and photochemical decomposition of AIBN and ACPA.

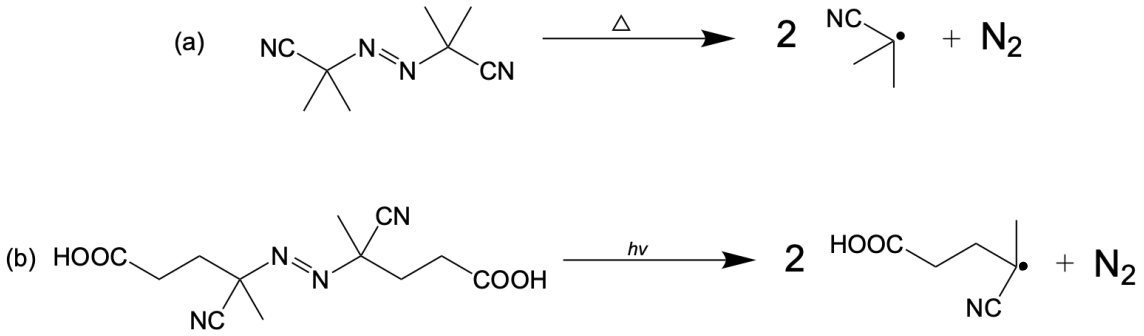


Figure 1.4. Homolytic cleavage of (a) AIBN and (b) ACPA via thermo and photolysis.

The selection for the initiator plays a very important role when conducting a thermal polymerisation. Typically, the rate constant for initiator decomposition (k_d) should be approximately 10^{-4} to 10^{-6} s^{-1}.[32] The half-life ($t_{1/2}$) is often used to express the decomposition rates of different initiators. The half-life describes the time taken for the initiator concentration to reduce to half its original value and is calculated using Equation 1.4. Initiators are often ranked according to the characteristic temperature at which their half-life is equal to 10 hours. For example AIBN has a 10 hour half-life of 65 °C, and ACPA has a 10 hour half-life of 68 °C.[33]

$$t_{1/2} = \frac{\ln 2}{k_d} \qquad \text{(Equation 1.4)}$$

The rate of thermal decomposition of the initiator is slow compared to the rate of monomer initiation. Therefore, the overall rate of initiation (R_i) for a thermal initiation can be expressed by Equation 1.5. this takes into account the rate constant for initiator decomposition (k_d), the initiator efficiency (f) and the generation of two radicals per initiator molecule. The initiator efficiency is defined as the ratio of the number of initiator molecules that start polymer chains, to the number of initiator molecules decomposed under the given conditions of the polymerisation. The rate of initiator decomposition is relatively slow; therefore, this step is considered the rate-determining step.

$$R_i = \frac{d[I\cdot]}{dt} = 2fk_d\,[I] \qquad \text{(Equation 1.5)}$$

The initiator radical ($I^{\bullet}$) then reacts with a vinyl monomer (M) to produce an active radical centre ($R^{\bullet}$). This active centre becomes the first macroinitiator and reacts with a monomer unit to become the propagating polymer radical ($P_n^{\bullet}$). The rate for the addition of each monomer is assumed to be independent of the chain length, this means, that all the

propagation steps have the same rate constant (k_p). Thus, the rate of polymerisation approximates to the consumption of monomer in the propagation step. Since both a monomer and the growing polymer chain are involved in the reaction, the reaction rate is proportional to both concentrations. The rate for the addition of each monomer unit (k_p) is assumed to be independent of DP, as outlined in Equation 1.6.

$$R_p = \frac{d[M]}{dt} = k_p\,[I][P_n\cdot] \qquad \text{(Equation 1.6)}$$

The propagation step would theoretically continue until all monomer units are consumed. However, pairs of radicals also tend to react with each other and thus annihilate their active centres. The termination can occur via combination or disproportionation. When chain termination occurs via combination, two growing polymer chains react with each other forming a single non-reactive polymer chain. The resulting polymer chain (P_{n+m}) has a molecular weight equal to the sum of the two polymer radicals (P_n + P_m). In contrast, if the termination occurs via disproportionation, a hydrogen atom is transferred from one radical to the other resulting in two polymers, one with a saturated end (P_m-H) and the other with an unsaturated end (P_n=) and each with an initiator fragment. As a result of these two termination mechanisms the molecular weight distribution of the final polymer can be relatively broad. These termination reactions occur to different extent depending on the structure of the monomer. Termination by combination is predominant for polystyrene (PS) chains,[34] whereas disproportionation is more common for poly(methyl methacrylate) (PMMA) chains,[35] both termination reactions are outlined in Figure 1.5.

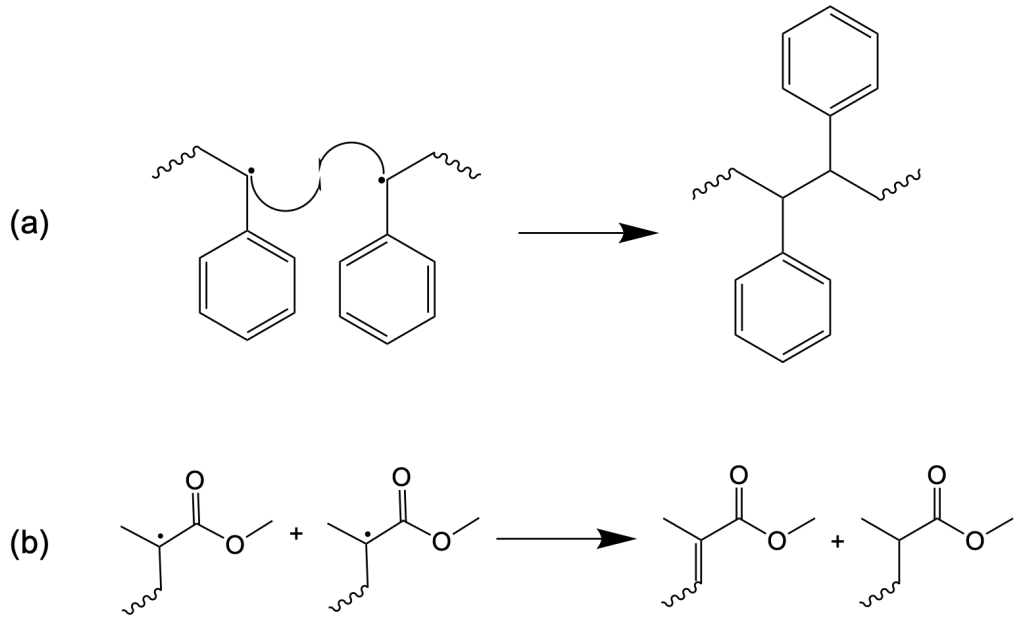


Figure 1.5. Example termination steps for (a) styrene and (b) methyl methacrylate, showing termination by combination and disproportionation, respectively.

Depending on the study being undertaken, there is often no need to distinguish between these two different types of termination reactions. The overall rate of termination (R_t) is given in Equation 1.7, where $k_t = k_{tc} + k_{td}$.

$$R_t = \frac{d[P\cdot]}{dt} = 2k_t\,[P\cdot]^2 \qquad \text{(Equation 1.7)}$$

The rate of termination is considerably faster than the rate of propagation.[36] therefore, in order to synthesise high molecular weight polymers, polymerisation must be performed under conditions where $R_t < R_p$. Equation 1.7 shows the R_i is second-order with respect to radical concentration and R_p is first order (Equation 1.6), to achieve high molecular polymers the radical flux is kept relatively low. During radical polymerisation, chain transfer reactions can also occur between the initiator, monomer solvent or dormant polymer chains. This is explained in detail in Section 1.2.3. These side reactions can result in cross linking or branching, thus impacting the dispersity and the final molecular weight of the polymer chains. These reactions don't have a significant impact on the overall rate of polymerisation. Instead, only the rate of polymerisation (R_{polym}), can be expressed by Equation 1.8.

$$R_{polym} = k_p\,[M]\sqrt{\frac{f k_d[I]}{k_t}} \qquad \text{(Equation 1.8)}$$

The kinetic chain length (v) is defined as the average number of monomer units consumed per active radical and is given by the ratio of the rate of propagation to the rate of termination.[32] For a thermally-initiated polymerisation, this can be calculated using Equation 1.9, and depends on the initiator efficiency (f) and the rate constants for initiator decomposition (k_d) , propagation (k_p) and termination (k_t).[32]

$$v = \frac{R_p}{R_t} = \frac{k_p[M]}{2\sqrt{f k_d k_t[I]}} \qquad \text{(Equation 1.9)}$$

The kinetic chain length can be used to calculate the degree of polymerisation (DP), this is dependent on the mechanism of termination, which can occur via combination (Equation 1.10) or by disproportionation (Equation 1.11). [8]

Combination $\quad DP = 2v \qquad$ (Equation 1.10)

Disproportionation $\quad DP = v \qquad$ (Equation 1.11)

Despite being widely used in industry, there are some significant drawbacks to radical polymerisation. In particular, control over the molecular weight distribution is difficult to achieve and it is impossible to synthesise pure block copolymers.[7] Broad molecular weight distribution result from the short life-time of the propagating chains (<<1 s), and the slow rate of initiation relative to the rate of propagation ($R_i < R_p$) which causes high molecular weight polymers to be formed early in the reaction.[36]

1.2.3. Chain transfer reactions

Chain transfer reactions are side reactions which result in deviation from the ideal kinetics of polymerisation. Termination of radicals normally occur by a collision between two active centres. Due to the chain length of the product in many systems being lower than expected scientists use the term kinetic chain length, v. If the mechanism for termination is solely responsible for limiting the kinetic chain length, it lies within the expected limits of v (disproportionation) and $2v$ (combination). In 1937, Flory [37] suggested that the attenuation of chain growth takes place if there is premature termination of the propagating chain by a transfer of activity to another species through a collision. Chain transfer reaction also occur between monomer, initiator, polymer and solvent.

1.2.3.1. Transfer to monomer

In some cases, the radical produced by chain transfer reaction can initiate the polymerisation of a different polymer chain. This is observed in reactions that are performed in the presence of various chemical substances containing functional groups with atoms of oxygen, nitrogen or sulfur, known as inhibitors. Inhibitors such as hydroquinone are normally added to prevent or at least retard the premature radical polymerisation of readily 30olymer30ed30le monomers. Transfer of a polymer radical to a monomer unit is achieved by hydrogen abstraction. If the radical formed in this reaction is virtually unstabilised by resonance, then the reaction with the parent unreactive monomer may produce little chain propagation. This is due to the tendency for stabilisation to occur by removal of hydrogen from the monomer. This leads to rapid chain termination and is known as degradative chain transfer. This is common for styrene, due to the stabilisation from the benzene ring.

1.2.3.2. Transfer to initiator

Organic peroxides are particularly susceptible to chain transfer reactions. The thermal decomposition of peroxide has been widely explored, the kinetic order of the decomposition is assumed to be unimolecular.[38,39] Further research from Nozaki and Bartlett [40] showed that the decomposition of benzoyl peroxide can be strongly induced by radicals present in the solution. As a consequence, a higher order accompanies the unimolecular decomposition. Figure 1.6 outlines the decomposition for a peroxide initiator. Products such as the benzoate radical, react with a variety of reaction solvents such as benzene. If the chain transfer reaction results in a new radical which is more stable and less reactive than the benzoate radical, the effect of the solvent should be supress the chain decomposition.

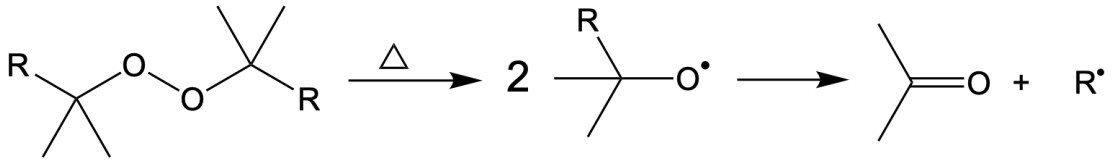


Figure 1.6. Chain transfer reaction and thermal decomposition of peroxide initiator.

1.2.3.3. Transfer to polymer

The transfer reaction with a polymer chain leads to branching rather than initiation of a new chain, so the average molar mass is relatively unaffected. The long and short chain branching detected in polyethylene is believed to arise from this mode of transfer. Chain transfer to polymer backbone in the polymerisation of acrylates is a well-researched topic. Ahmad *et.al* [41] suggested the backbone radical resulted in monomer addition leading to branching in polyacrylates. Chain transfer in a polymer backbone can occur via two different pathways: (a) through intramolecular hydrogen abstraction (backbiting) or (b) through intermolecular hydrogen abstraction. Chiefar *et al*.[42] suggested a pathway which could be used to produce macro-monomer for block and graft copolymer formation. The mechanism was believed to consist of a chain transfer to polymer backbone and β-scission to produce the macromonomer and a new propagating radical. In their research they first conducted an experiment on the hydrogen abstraction process in poly(butyl acrylate) using a thermal initiator with different monomer concentration at elevated temperatures. The results showed at lower monomer concentration the intramolecular hydrogen abstraction dominates. At lower monomer concentration, the rate of propagation is reduced, therefore leading to the production of macromonomers with low molecular weight. At higher monomer concentration the intermolecular hydrogen abstraction mechanism was more important. The results showed the molecular weight of the macromonomer decreases by increasing the reaction temperatures is mostly likely due to backbiting hydrogen abstraction and fragmentation.

This is very common in ethylene homo-polymerisation where increasing the temperatures results in an increase in the tendency of backbone hydrogen abstraction. Figure 1.7 outlines a scheme for β-scission and intermolecular hydrogen abstraction between polymers and monomer.

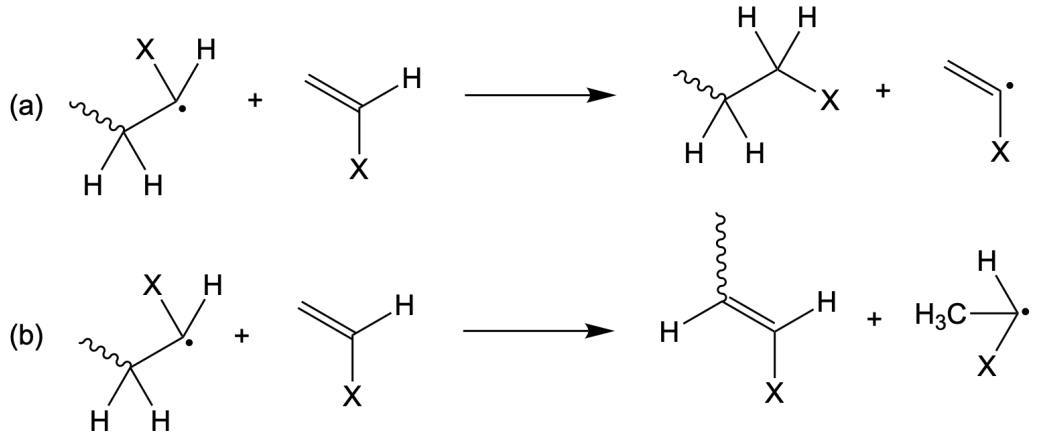


Figure 1.7. Chain transfer reaction between polymer chains and monomer units via (a) H abstraction and (b) β-scission

1.2.3.4. Transfer to solvent

The effect solvent has on the rate of polymerisation has been widely studied by a variety of researchers. Depending on the solvents used, increasing and decreasing the solvent concentration leads to deviations in the ideal kinetics of radical polymerisation.

The reactivity and structure of the solvent and the reactivity of the radicals formed by addition or transfer governs retardation. Schulz & Husemann[43] and Kamenskaya & Medvedev[38] originally proposed the formation of a complex between the initiator and monomer to explain the retardation in polymerisation. The following researchers proposed a mathematical equation which takes into account orders greater than unity, with respect to monomer. Matheson[44] composed a different theory to the above researcher. In his expression he considered, an initiator molecule splits into two fragments, they are surrounded by a physical "cage" of solvent or monomer molecules. As a result, they may suffer many collisions, leading to side products, before they diffuse out of the cage. This idea was strongly criticised by Flory[37] who believed that it was based on unrealistic interpretation of the rate of the process involved.

Burnett and Melville [45] outlined three ways in which a radical produced from the solvent may react. Firstly, the solvent radical produced is very reactive and reinitiates to form a new chain without any time lag. Secondly, the radical is relatively unreactive, due to resonance stabilisation and can only reinitiate slowly, thus reducing the overall rate. Finally, the radical may be destroyed with another of its kind or a polymer radical. Burnett *et al*.[46,47] reported

that the rate of polymerisation of MMA in the presence of halogenated benzene and naphthalene was larger than expected if the solvents were inert diluents. The increase in rates was not accompanied by an increased inclusion of initiator, and there was no presence of solvent fragments in the polymer. Burnett *et al*. suggested that an increase in the rate of polymerisation was due to an enhanced rate of initiation. It was discovered that in solvents which showed a rate-enhancing effect, there was an increase in the efficiency of initiator as measured by the inhibitor technique, although there did not appear to be any dependence on increasing the solvent concentration.

A significant decrease to polymer chain length is often observed when polymerisation is carried out in solution rather than in the bulk undiluted state, this variation is a function of both the extent of dilution and the type of solvent used. The effectiveness of a solvent in a transfer reaction depends on the concentration, the strength of the bond involved in the abstraction step, and the stability of the solvent radical formed. Brienbach and Maschin[48] carried out the polymerisation of styrene in carbon tetrachloride; their results showed that the polymers produced contained chlorine atoms. The results suggested the use of halogenated solvents results in the transfer of halogen atoms. The chain transfer reaction between the polymer radical and carbon tetrachloride is shown in Figure 1.8.

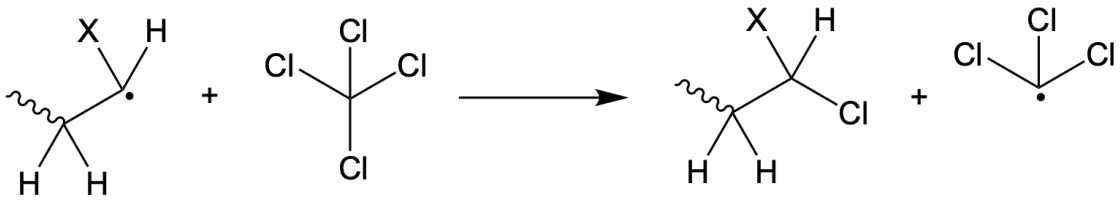


Figure 1.8. Chain transfer reaction between a polymer radical and carbon tetrachloride.

1.2.4. Controlled radical polymerisation

Controlled radical polymerisation (CRP) techniques represent the most versatile and facile approach for block copolymer synthesis, due to their compatibility with a wide spectrum of monomers, high tolerance of functional groups, limited impurities, and ease of experimental setup. The main methods used to produce polymers with low dispersity are CRP techniques and anionic polymerisation. The most well-known CRP techniques are the following; reversible addition fragmentation chain transfer (RAFT) which uses dithiocarbonyl derivatives as a charge transfer agent (CTA);[49] Atom transfer radical polymerisation (ATRP) which involves alkyl halides, metallic salts and ligands;[50] and nitroxide-mediated polymerisation (NMP) which requires alkoxyamines.[51] In the past few decades, we have seen the rapid growth in the development of new techniques which offer similar characteristics, in the form of using alkyl halides as transfer agents..

In controlled radical polymerisation, the main goal is to suppress the rate of termination compared to the rate of propagation.[36] This is achieved by controlling the propagation step in radical polymerisation by adding a variety of compounds. The propagation step involved in a few controlled radical polymerisations uses degenerative transfer (DT) of an atom or a group.[52] The reaction scheme for this type of reaction has been outlined in Figure 1.9. where X represents the transferable atom or group, P_m and P_n represent polymer chains and M represents the monomer unit.

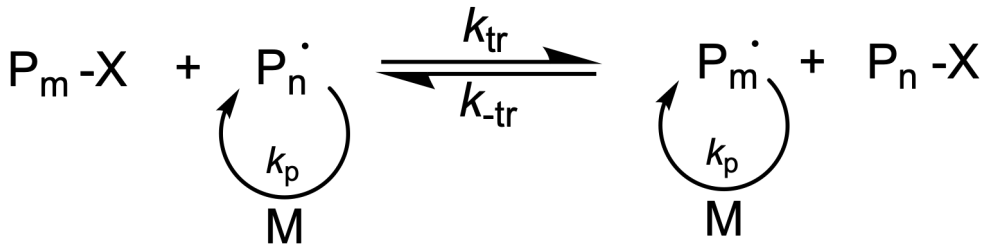


Figure 1.9. Reaction scheme for the propagation step involved in controlled radical polymerisation reaction which follows a degenerate transfer mechanism.[52]

1.2.4.1. Atom transfer radical polymerisation

Atom transfer radical polymerisation (ATRP) processes have evolved significantly during the past 15 years.[53] The original ATRP started with equivalent concentration of alkyl halide and a catalyst with the transition metal in a lower oxidation state (Mt^n/L, the transition metal species, Mt in oxidation state *n* and L represents a ligand), the reactions were carried out in bulk or in organic solvents. ATRP can be used to produce polymers with controlled molecular weight, low dispersity (M_w/M_n < 1.1), and controlled molecular architecture in terms of chain topology (stars, cycles, combs, brushes, regular networks) and composition (block, graft, alternating, gradient copolymers).[54] However, the ATRP catalysts used,

currently limit the application of ATRP from using acidic monomers and dienes. Acidic monomers can protonate ligands and destroy the catalyst complexes.

Through further research, a “reverse” ATRP was developed that started by adding the transition metal complex in its higher oxidation state, X–Mt^{n+1}/L, which was then changed to the activator (Mt^{n}) by reaction with a conventional radical initiator.[55] This change permitted starting ATRP with oxidatively stable but more sensitive complexes that were reduced to the activator state *in situ*. Consequently, the process could only be used for the preparation of homopolymers and not for block copolymers or systems with a complex architecture.

ATRP is controlled by an equilibrium between propagating radicals and dormant species, mainly from initiating alkyl halides/ macromolecular species (P_nX). The dormant species regularly react with the rate constants of activation (k_{act}) with the transition metal complexes in their lowest oxidation state, Mt^{m}/L which act as activators to form growing radicals ($P_n^{\bullet}$), and deactivator-transition metal complexes in their higher oxidation state, attached with halide ligands X-Mt^{m+1}/L. the deactivator reacts with the propagating radical in a reverse reaction (k_{deact}) to recreate the dormant species and the activator. Figure 1.10 outlines the equilibrium presents in an ATRP mechanism.

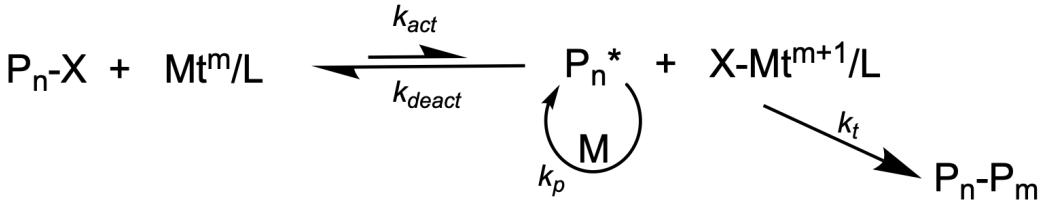


Figure 1.10. Equilibrium present for ATRP polymerisation.[55]

1.2.4.2. Nitroxide mediated polymerisation

Nitroxide mediated polymerisation (NMP) is based on a reversible termination mechanism between growing propagating macro radicals and a nitroxide, which acts as a control agent, to yield a macro alkoxyamine as the predominant species. This dormant functionality generates back the propagating radical and the nitroxide by a simple homolytic cleavage by temperature increase. Following this an equilibrium between dormant and active species, an activation-deactivation equilibrium is established. The benefits to the establishment of this equilibrium, is it being dictated by thermal conditions and doesn’t require the addition of a catalyst or a bimolecular exchange being required.

NMP is thermally sensitive due to the reversible thermal C-O bond cleavage of a polymeric alkoxyamine to generate the corresponding polymeric radical and a nitroxide. Monomer insertion with subsequent nitroxide trapping leads to chain-extended polymeric

alkoxyamine. The whole process is controlled by the Persistent Radical Effect (PRE).[56] PRE is a general principle that explains the highly specific formation of the cross-coupling products (R^1-R^2) between two radicals R^1 and R^2 when the nitroxide, the polymeric radical, and the two radicals are formed at equal rates. Figure 1.11 outlines the mechanism involved in NMP polymerisation. The equilibrium constant (k) between the dormant alkoxyamine, the polymeric radical and the nitroxide is a key parameter of the polymerisation process. The equilibrium constant K is defined as k_d/k_c (k_d = rate constant for alkoxyamine C-O bond 36olymer36e; k_c = rate constant for formation of the polymeric nitroxide). Parameters such as steric factors, H-bonding and polar effects influence the K value.[57]

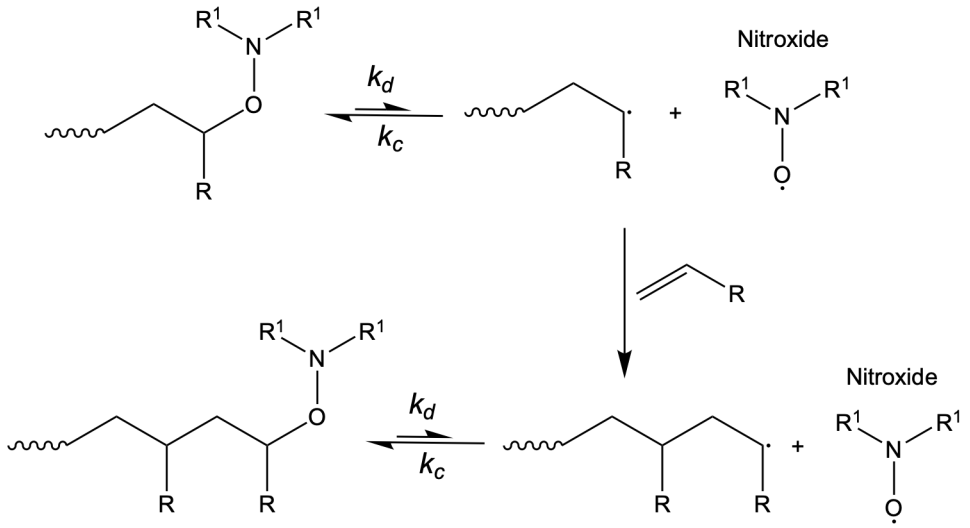


Figure 1.11. Reaction scheme for NMP polymerisation. [57]

NMP has been used with great success to prepare a wide range of polymers with different composition and architectures. The key advantages of using ATRP are the following: the simplicity of conducting the polymerisation, NMP is compatible with a wide range of monomer and the purity of the final polymer.[58] The main challenges in NMP are the following: Slow polymerisation kinetics that require high temperatures and lengthy polymerisation times, the polymerisation of methacrylate monomers using NMP is difficult due to side reactions and/or slow recombination of the polymer radical with nitroxide. Side reactions can limit molecular weight and broaden polymer molecular weight distribution under certain NMP conditions, including cleavage of the alkoxyamine N-O bond, rather than the desired NO-C cleavage,[59,60] chain transfer to solvent,[61] unproductive nitroxide decomposing [62] and oxidation of alkyne-bearing monomer.[63]

1.2.4.3. Reversible addition fragmentation chain transfer polymerisation

Reversible addition fragmentation chain transfer (RAFT) was first discovered by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) in 1998.[49] The technique is widely utilised in industry, due to its versatility to a range of monomers and that it can be conducted in both organic[64] and aqueous[65] solution. One of its most important features is the control over the molar mass and low dispersity (often <1.2) of the final polymers produced. The control from this technique is associated with the addition of a thiocarbonylthio CTA[49] which has been referred to as a RAFT agent[66] in the literature. The structure of the CTA is shown in Figure 1.12. The CTA contains a reactive C-S bond which regulates the polymer molecular weight[66] via transferring between dormant polymer chain and the growing chain through addition & defragmentation steps. This step is referred to as chain equilibrium.

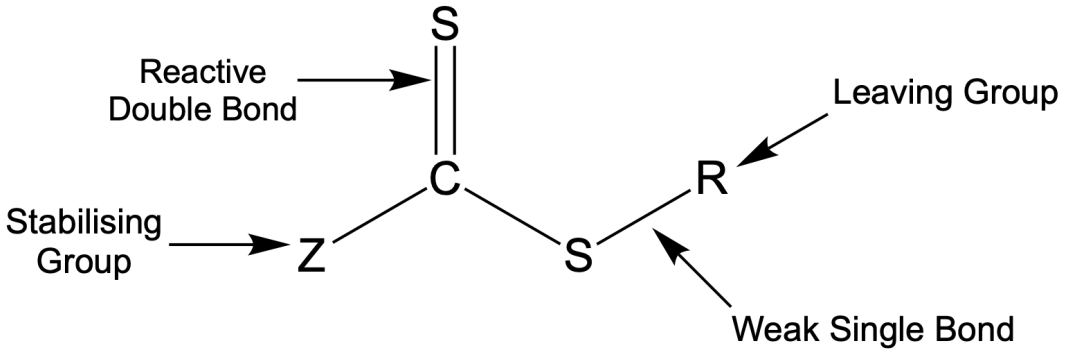


Figure 1.12. Chain transfer agent used in reversible addition fragmentation chain transfer (RAFT) polymerisation.[67]

Vinyl monomers can generally be divided into two classes; more activated monomers (MAMs) or less activated monomers (LAMs). The classification is based on the ability of the monomer to react during the polymerisation. For MAMs the vinylic group is conjugated to a neighbouring functionality such as a carbonyl group or an aromatic ring. The vinylic group in LAMs are normally adjacent to an electron rich atom, such as oxygen or nitrogen.[68] The polymerisation of MAMs is generally well controlled through the use of active CTAs which provide a high rate of reversible chain transfer via addition-fragmentation with respect to propagation. Therefore, less active CTAs provide better control over LAMs. The Z-group in RAFT agents such as xanthates and dithiocarbamates donate electron density into the thiocarbonyl group by zwitterionic resonance. As a result, the reactivity of the thiocarbonyl towards the propagating radical is deactivated and the RAFT radical intermediate is destabilized.[69]

Another important feature is the structure of the R and Z group on the CTA. Both groups play an important role when obtaining control of the polymerisation for different monomers. The Z group is known as the stabilizing group,[67] the reactivity of the thiocarbonyl group towards radical addition is dictated by this group. The R-group on the RAFT agent is referred to as the leaving group. In RAFT polymerisation the R-group must be a good homolytic leaving group with respect to the propagating radical and must be able to reinitiate addition-fragmentation. Steric factors, radical stability, and polar effects are significant in determining the leaving ability of an R group.[70] The R group plays an important role when preparing block copolymers via a two-step synthesis. The structure of the R group is normally a secondary or tertiary carbon.

In CRP radical polymerisations, we can produce copolymers by sequential monomer additions.[71] This is a common method used in RAFT polymerisation where the homopolymer produced using RAFT, acts as the macroCTA for the polymerisation of the second monomer. When synthesising a block copolymer, the order in which the monomers are incorporated into the copolymer is important as the first block serves as a macro-R group during the polymerisation of the second monomer. Therefore, the macro-R group must be a good homolytic leaving group with respect to the propagating radical of the second monomers.

1.3. LITERATURE REVIEW ON ALKYL HALIDES USED IN RADICAL POLYMERISATION

In addition to the CRP techniques mentioned earlier, the use of haloalkanes which follow a typical degenerate transfer reaction has gained some attention. The most well-known haloalkane used in polymerisation currently are derivates of iodoalkanes, due to the strength of a carbon-halogen bond. Table 1.1 outlines the bond length and bond strength for fluoroform, chloroform, bromoform and iodoform. The bond strength for the C-I bond in iodoform is relatively low which allows for the production of radicals.[72] The table shows, In terms of bond strength in the halogen series carbon fluoride bonds has the strongest bond due to its high electronegativity and short bond length. Due to this reason, fluorinated haloalkanes tend to be very stable and unreactive. Near the bottom of the series, we have Astatine, As. Haloalkanes containing this group are known to be carcinogenic.

Table 1.1. Carbon-halogen bond length and bond strength for fluoroform, chloroform, bromoform, and iodoform.[73]

Carbon halogen bond	Bond length of carbon-halogen (Å)	Bond strength of carbon-halogen (kcal)
C-F	1.332	114.3
C-Cl	1.767	78.0
C-Br	1.930	66.5
C-I	2.128	53.2

1.3.5. Iodine Transfer Polymerisation

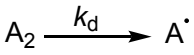
Iodine Transfer Polymerisation (ITP) was first discovered in the 1970s by Tatemoto.[74] the mechanism involved is similar to the RAFT polymerisation, due to the requirement of a CTA. The CTA involved in ITP is based on iodocompounds, as iodine atom are good leaving group. In radical polymerisation, the iodine atoms are transferred onto growing macromolecular chains.

ITP was first discovered In 1978 by Tatemoto[74] from using the initiating radical, iodoflurocompounds which could enter in a controlled process, based on a degenerate transfer. Tatemoto discovered this method from using fluoroolefin monomers but were then extended to using other non-halogenated vinyl monomers. Stark[75] published a paper on telomerisation reactions, in which he explained the activity of telogens towards chain transfer depends on the nature of the atom being abstracted and the substituents on the telogen that stabilises the telogen radical. He proposed a decrease for the halogens I > Br > Cl ~ H. Stark stated that primary end groups are less effective than secondary ones.

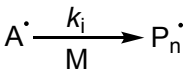
In degenerate chain transfer, the key parameters are the concentration of the transfer agent (controls the molecular weight of the polymer) and the chain transfer rate constant (higher the k_{exch} value, lower the dispersity of the polymer chains). The mechanistic steps for ITP have been outlined in Scheme 1.1. The mechanism outlined consists of 4 steps: Initiation, chain transfer, propagation and termination. The first step involves the generation of the initiating radical ($I^{\bullet}$). This is normally achieved by the thermal decomposition of an initiator such as AIBN. For polymers with iodine end groups, the radical can be generated by photodissociation of the C-I bond, to produce $P^{\bullet}$ and $I^{\bullet}$ radicals. The initiating radicals then add on to the first monomer unit to form the macro-radical. In ITP the exchange of iodine from the alkyl halide transfer agent (R-I), to the propagating radical ($P_n^{\bullet}$), results in the formation of the polymer alkyl iodine (P_n-I), and a new initiating radical ($R^{\bullet}$). the new initiating

radical generated from the alkyl iodide or the $P_n^{\bullet}$, adds onto a monomeric unit and propagates. The final step involves the termination of the radical, which can be either by combination or disproportionation.

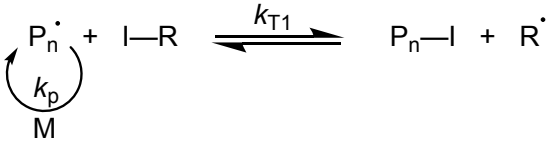
Decomposition of (A_2) Initiator:



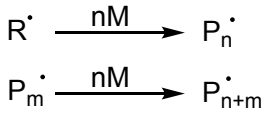
Initiation:



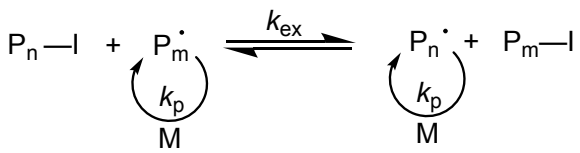
Chain Transfer:



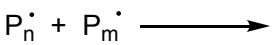
Propagation:



Equillibrium between dormant and propagation species (Degenerative Transfer):



Termination:



Scheme 1.1. Reaction scheme for ITP where (*A*) represents the initiator, (*M*) represents the monomer, © represents the alkyl group from the chain transfer agent, (P_n) and (P_m) represent growing polymer chains.[76]

Lansalot *et al.*[77] conducted a variety of polymerisation using derivatives of styrene with iodoform. The researchers suggested PS can be produced with controlled M_n about 15000 g/mol using iodoform, which behaves as a transfer agent. Lansalot's research focused on the production of low molar mass polymers which improved polymer solubility. It was reported that a concentration above 0.2 wt/% of iodoform gave good control over molar mass. However, when the concentration is above 1 wt/% a delay in the polymerisation was normally observed.

C. Barson,[78] and S. Mah[79] suggested iodoform behaves as an effective transfer agent. Mah, S suggested, the iodine atoms in iodoform induce a very strong inductive effect, which lowers the activation energy and allows the rate of transfer to be equivalent to the rate of propagation. This could suggest polymerisation reactions using bromoform could behave similarly.

More recently, Percec *et al.*[80] used iodoform as an initiator in the polymerisation of vinyl chloride. The major difference in Percec's research was the use of a transition metal in its zerovalent oxidation state, for example, $Cu^{(0)}$. Following this many other attempts were made to improve the method. In a later study, Percec[81] changed the metal complex to one in its monovalent oxidation state. The reactions were conducted in a two-phase system consisting of THF and water.

1.3.6. Chlorinated haloalkanes used in radical polymerisation

In 1962, H. George and F. Onyon[82] were able to polymerise styrene using carbon tetrachloride. The polymerisation using carbon tetrachloride resulted in polymers containing CCl_3 end groups, which was identified through gravimetrical analysis. From the experiments conducted they were able to notice increasing the concentration of carbon tetrachloride in the system resulted in a decrease to the degree of polymerisation and the rate of polymerisation. However, when the results were plotted using the Gregg-Mayo equation they noticed a deviation from the expected linear plot. The researchers suggested the traces of impurities acted as retarders, which reacted with the primary radicals that resulted in deviations from the expected results.

M. Matsuda, Y. Ishioroshi and T. Hirayama[83] have researched heavily into polymerising a variety of monomer in the presence of halogenated alkanes. In 1966, they reported organic halides such as carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) played an important role in the polymerisation of *N*-vinylcarbazole, styrene and MMA. Their research showed that the polymerisation of *N*-vinylcarbazole was possible at room temperature without using an initiator. Liquid sulfur dioxide pyridine was added which was later discovered to form a complex with carbon tetrachloride. From further studies, Matsuda *et al*. noticed that the polymerisation does not proceed without the presence of carbon tetrachloride.

In 1967, M. Matsuda and Y. Ishioroshi[84] reported the polymerisation of MMA, is extremely favoured when carbon tetrachloride and liquid sulfur dioxide was present as an electron acceptor and additives. It was discovered the addition of a stable radical molecule, 2,2-diphenyl-1-picrylhydrazyl (DPPH) caused retardation to the polymerisation of MMA. The results suggested the existence of a radical intermediate in a system containing poly-2-VP, sulfur dioxide, carbon tetrachloride and styrene.

1.3.7. Brominated haloalkanes used in radical polymerisation

In 1953, A. Dunn, B. Stead and H. Melville[85] were able to produce block copolymers using haloalkanes under a range of conditions. Dunn *et al*. produced styrene and MMA block copolymer using carbon tetrabromide (CBr_4) and bromo-trichloromethane (CCl_3Br). According to Dunn, CCl_3Br behaved as a photosensitizer and a transfer agent in the polymerisation of styrene. They reported that the polymer possessed bromine and trichloromethyl end-groups which could undergo further polymerisation to form block copolymers. It was discovered from using different concentration of carbon tetrabromide, the rate was found to fall off rapidly with time**.** They concluded the main reason for this phenomenon was due to competing side reactions at high temperatures.

K.Thananukul *et al.*[1] explored the use of bromoform in the photopolymerisation of acrylamides in aqueous solution. The report suggested, bromoform behaves as a CTA in the photopolymerisation of acrylamide. Their argument was supported by kinetic plots which showed increasing bromoform concentration, resulted in the formation of low molar mass polymer and a decrease to the apparent rate constant. In their research, monomer conversion was calculated using the weight of recrystallised polymer at specific time intervals and molar mass data was estimated from dilute-solution viscometry flow-time measurements. The research consisted of four different experiments: A negative control, a polymerisation reaction using 0.5 mol % of $CHBr_3$ as a photoinitiator and two reactions using ACPA as a photoinitiator with 0.5 and 2.0 mol % of $CHBr_3$ as a CTA. The report concluded chain transfer to bromoform occurs by both *Br* and *H* atom transfer. The $CHBr_2^{\bullet}$ radical was assumed to be less reactive compared to the $Br^{\bullet}$ radical. The report suggested *Br* transfer leads to *Br*-terminated chains in which the terminal C-Br bond can re-dissociate leading to re-initiation and re-propagation of the same chain,.

In 1961, M, L Miller[2] used bromoform to produce polyacrylamides and acrylamide-acrylonitrile block copolymers. Miller's research was based on Dunn *et al.*[85] research, which used carbon tetrabromide. Miller's research involved using tubes of acrylonitrile monomer with bromoform and exposing them to general electric lamp to produce acrylonitrile polymer. Miller focused on using the measurements from the intrinsic viscosities of the polymer. Miller concluded that the technique offered the opportunity to synthesise copolymers which could contain two to three long blocks.

In Miller's view, bromoform acted as a photo-initiator in the polymerisation of the acrylonitrile. He suggested the first step involved the photolysis of bromoform to produce $Br^{\bullet}$ and $CHBr_2^{\bullet}$ radicals. Miller stated that both radicals can produce the polymer macro-radicals. The paper suggested the liberation of a radical from the photodissociation of the macro-radical could initiate other chains. The polyradicals could, therefore, terminate by combination with one another, combination with $Br^{\bullet}$ or disproportionation. Miller suggested polymers with labile bromine end groups can be 43olymer43ed to produce block copolymers by the addition of acrylamide monomer.

In literature, there has been a variety of articles on the photodissociation of bromoform. Using the emission spectrum of bromoform, McGivern *et al.*[86] concluded that C-Br bond fission was the primary dissociation channel. The $CHBr_2$ fragments were produced with sufficient internal energy to undergo secondary dissociation, producing both CHBr and Br or CBr and HBr with quantum yields equal to 0.3 and 0.4, respectively. For McGivern's research photofragment translational spectroscopy (PTS) was conducted at 193 nm with a vacuum ultra violet (VUV) ionisation detection.

The CHBr fragment has been widely studied by Sears *et al.* [87,88] and Liu *et al.*[89] using the photodissociation of bromoform and transient frequency modulation spectroscopy. Liu *et al*. [89] suggested that the CHBr radicals from the photodissociation of bromoform at 266 nm were significantly more energetic than those produced at 193 nm. The results suggested that the CHBr fragments at 266 nm may arise from a multiphoton process because the energetics of CHBr formation via one photon at 193 nm. Due to spontaneous secondary dissociation of $CHBr_2$, via Br_2 elimination at 266 nm should be similar.

Zou *et al.*[90] explored this further by using VUV-ionisation photofragment translational spectroscopy at 248 nm. They concluded that the C-Br bond fission is the dominant and most important single-photon dissociation channel of bromoform. In addition to primary Br and $CHBr_2$ signals, they also observed Br, CHBr, CBr, HBr and Br_2 products which are from the secondary photodissociation of $CHBr_2$ and CHBr.

1.4. AIMS

The purpose of this research project is to determine the role bromoform plays in radical polymerisation. Work reported in the literature suggests that bromoform behaves as a CTA[1] and a photoinitiator[2] under UV conditions. Due to this uncertainty, further research is required to determine the true mechanistic role of bromoform. For this project, the behaviour of bromoform under thermal conditions have also been explored. An advantage to this route is the low purchasing price of bromoform compared to other CTAs. The role of bromoform was identified under both UV and thermal conditions. The experiments were conducted under non-aqueous systems, to tackle the gel effect and hot spots.[91] The main focus was on hydrophobic monomers, such as styrene and MMA. Due to the production of PMMA-PS block copolymer have been using a variety of polymerisation techniques,[88,89] for this reason, the PMMA-PS copolymer will be prepared using the bromoform-mediated polymerisation.

The aims for this research project:

1. Identify the role of bromoform in the polymerisation of hydrophobic monomers under both UV and thermal conditions in an organic solvent.
2. Use the bromoform-mediated polymerisation technique to produce block copolymers under a range of conditions.
3. Characterise block and homopolymers using a range of analytical techniques.

To learn the synthetic techniques involved in this project, a trial polymerisation was conducted. Due to RAFT polymerisation being widely used and explored, the first reaction conducted was the RAFT polymerisation of styrene under thermal conditions. To achieve the aforementioned objectives a variety of experiments were designed and conducted to identify the conditions required for the synthesis of block copolymer. The variable altered included; the quantity of bromoform and initiator added, and the reaction conditions used for the polymerisation. A series of characterisation techniques were employed to characterise the polymers produced.

CHAPTER 2

MATERIALS AND EXPERIMENTAL METHODS

2.1. MATERIALS

Styrene (≥ 99 %, containing 0.5 ppm 4-*tert*-butylcatechol as a stabiliser), methyl methacrylate (MMA) (≥ 97 % containing 0.5 ppm 4-*tert*-butylcatechol as a stabiliser), 2,2′-azobis(isobutylnitrile) (AIBN) (≥ 98 %), 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) (≥ 97 %), tetrahydrofuran (THF) (≥ 99.9 %, HPLC grade inhibitor free) and 4'-azo-bis(4-cyanopentanoic acid) (ACPA) (≥ 99.0 %) were obtained from Sigma Aldrich. Methanol (MeOH), water (H_2O), THF (≥ 97 %, HPLC grade), triethylamine (TEA, ≥ 97 %), bromoform (≥ 96 %, stabilized), were purchased from Fischer Scientific and were all laboratory reagent grade. Chloroform-d ($CDCl_3$) (99.8 % At + 0.05 % trimethylsilane, TMS) and acetone-d6 (CD_3COCD_3) (99.9 % At + 0.05 % TMS) were obtained from Goss scientific. The styrene and MMA both contained inhibitor which was removed by passing through a basic alumina column. AIBN was recrystallized from methanol and stored below room temperature.

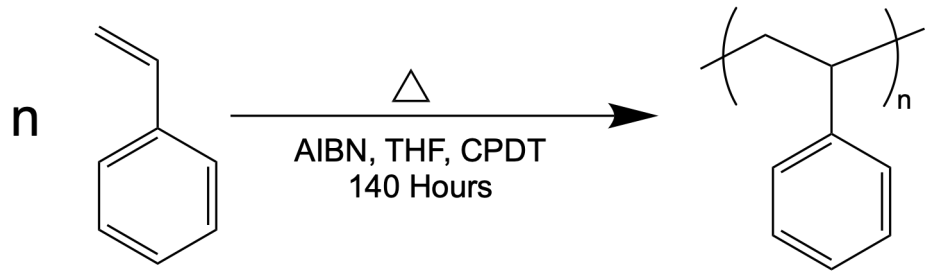
The ultra-violet (UV) light source was a commercially available UV lamp (Philips solarium model MD1-15) comprising of 4-parallel, 15-watt fluorescent tubes which emits UV light in the wavelength range of 100-400 nm. The UV lamp was placed in an aluminium box.

2.2. EXPERIMENTAL METHODS

In this research project the focus was on the polymerisation of styrene and MMA in non-aqueous media. The kinetics of each reaction was studied by monitoring the monomer conversion using ^{1}H NMR, and molar mass progression using GPC throughout the reaction. This was achieved by taking multiple samples from the reaction mixture at different intervals.

2.2.1. Synthesis of PS via RAFT polymerisation

The following method describes the synthesis of PS with a target degree of polymerisation of 40 via RAFT polymerisation, as depicted in Scheme 2.1.

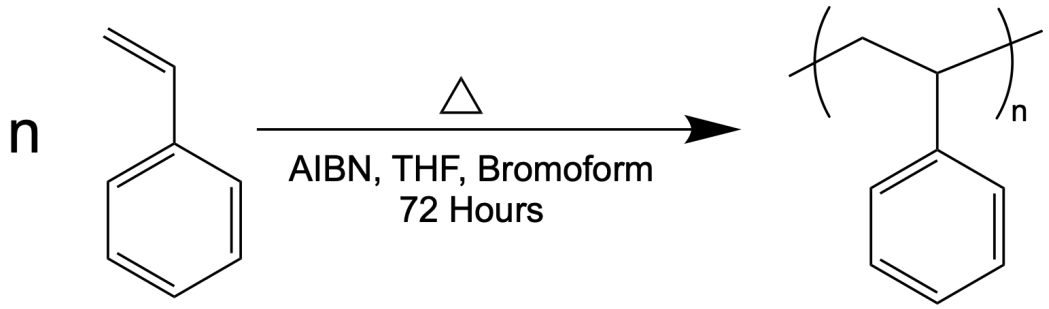


Scheme 2.1. RAFT polymerisation of 2 g (19.2 mmol) styrene with a target degree of polymerisation 40 using 15 mg (0.1 mmol) AIBN, 17 mg (0.5 mmol) CPDT in 5 mL THF at 70 °C for 140 hours.

2 g (19.2 mmol) styrene and 15 mg (0.1 mmol) AIBN were weighed into a 25 mL round bottom flask containing 5 mL of THF with 17 mg (0.5 mmol) CPDT. The reaction flask was then sealed with a rubber septum containing a magnetic stirring bar. Following this, the mixture was stirred for 30 mins, then degassed 3 times via vacuum and nitrogen cycles. The reaction mixture was sealed under nitrogen and immersed in a 70 °C preheated oil bath. At timed intervals, two samples of 20 μL of the reaction mixture were withdrawn using a pipette for kinetic studies (during this operation a stream of nitrogen was introduced, and ventilation was provided). The two samples were used to calculate monomer conversion and the molar mass of the polymer using ^{1}H NMR and GPC, respectively. As the reaction proceeded the solution became viscous, and after 140 hours, the polymerisation was terminated by unsealing the flask and quenching the flask in ice. The resulting polymer was dissolved in 5 mL THF and added dropwise to stirred cold methanol (100 mL). Excess methanol was decanted and the polymer was collected by filtration using a Buchner funnel to yield a yellow solid. The solid was then ground into a powder using a pestle and mortar and then dried overnight on the vacuum pump.

2.2.2. Synthesis of PS using bromoform under thermal conditions

The following method describes the synthesis of PS under thermal conditions using variable quantities of AIBN and bromoform, as depicted in Scheme 2.2.



Scheme 2.2. Preparation of PS using 5 g (48 mmol) styrene with variable but known, quantity of AIBN and bromoform in 10 mL THF. The reactions were conducted in a 70 °C oil bath.

5 g (48 mmol) styrene and AIBN were weighed into a 50 mL round bottom flask containing 10 mL of THF with a variable but known, concentration of bromoform. The reaction flask was then sealed with a rubber septum containing a magnetic stirring bar. Following this, the mixture was stirred for 30 mins, then degassed 3 times via vacuum and nitrogen cycles. The reaction mixture was sealed under nitrogen and immersed in a 70 °C preheated oil bath. At intervals of 1 h, two samples of 20 μL of the reaction mixture were withdrawn using a pipette for kinetic studies (during this operation a stream of nitrogen was introduced, and

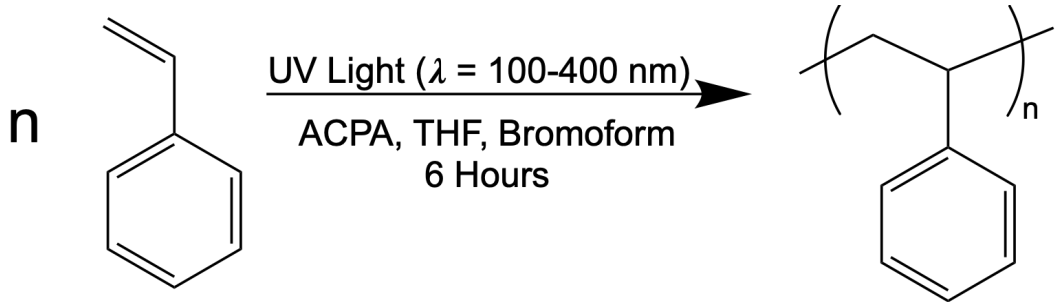
ventilation was provided). The two samples were used to calculate monomer conversion and the molar mass of the polymer using ^{1}H NMR and GPC, respectively. As the reaction proceeded the solution became very viscous, and after 72 hours, the polymerisation was terminated by unsealing the flask and quenching the flask in ice. The resulting polymer was dissolved in 10 mL THF and added dropwise to stirred cold methanol (200 mL). Excess methanol was decanted and the polymer was collected by filtration using a Buchner funnel to yield a white solid. The solid was then ground into a powder using a pestle and mortar and then dried overnight on the vacuum pump.

Table 2.1. Preparation of PS using 5 g (48 mmol) styrene and the variable quantities of bromoform and AIBN listed below in each experiment in 10 mL THF. The reactions were conducted at 70 °C for 72 hours, e.g. styrene:bromoform:AIBN = 40:1:0.2

Experimental Code	Molar equivalents of bromoform added	Mass of bromoform added (g)	Molar equivalents of AIBN added	Mass of AIBN added (g)
MOZ 05	0.0	0.000	0.0	0.000
MOZ 06	1.0	0.304	0.0	0.000
MOZ 07	0.0	0.000	0.2	0.039
MOZ 13	0.5	0.152	0.2	0.040
MOZ 14	1.0	0.305	0.2	0.039

2.2.3. Synthesis of PS using bromoform UV conditions

The following method describes the synthesis of PS under UV conditions using variable quantities of ACPA and bromoform, as depicted in Scheme 2.3.



Scheme 2.3. Preparation of PS under UV conditions using 5 g (48 mmol) styrene with variable but known**,** quantity of ACPA and concentrations of bromoform in 10 mL THF.

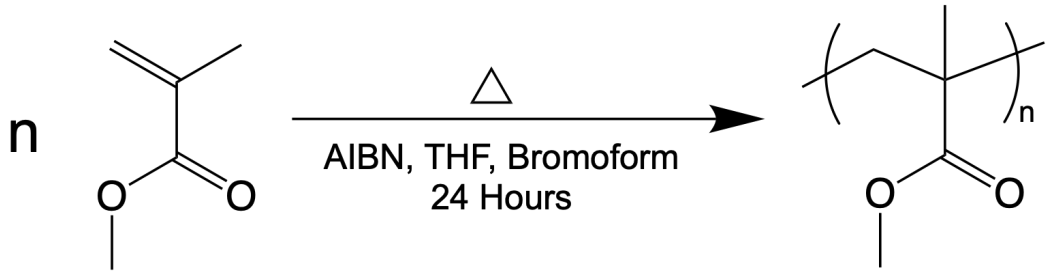
5 g (48 mmol) styrene and ACPA were weighed into a 50 mL round bottom flask containing 10 mL of THF with a variable but known, concentration of bromoform. The reaction flask was then sealed with a rubber septum containing a magnetic stirring bar. Following this, the mixture was stirred for 30 mins, then degassed 3 times via vacuum and nitrogen cycles. The reaction mixture was sealed under nitrogen and then placed in the aluminium box by balancing on a clear dish. The UV lamp was placed on top of the box, the distance between the flask and the lamp was roughly 15 cm. The UV lamp was switched on for 6 hours. At intervals of 1 h, two samples of 20 μL of the reaction mixture were withdrawn using a pipette for kinetic studies (during this operation a stream of nitrogen was introduced, and ventilation was provided). The two samples were used to calculate monomer conversion and the molar mass of the polymer using ^{1}H NMR and GPC respectively. The reaction was terminated after 6 hours by unsealing the flask and quenching into ice. The resulting polymer was added dropwise to stirred cold methanol (200 mL). Excess methanol was decanted and the polymer was collected by filtration using a Buchner funnel to yield white solid. The solid was then ground into a powder using a pestle and mortar and then dried overnight on the vacuum pump.

Table 2.2. Preparation of PS under UV conditions by irradiating the reaction flask with UV light (λ = 100-400 nm) for 6 hours. The reaction flasks contained 5 g styrene and different quantities of ACPA and bromoform (listed below for each experiment) in 10 mL THF, e.g. styrene:bromoform:ACPA = 40:1:0.2

Experimental Code	Molar equivalents of bromoform added	Mass of bromoform added (g)	Molar equivalents of ACPA added	Mass of ACPA added (g)
MOZ 08	0.5	0.152	0.2	0.067
MOZ 09	0.0	0.000	0.0	0.000
MOZ 10	1.0	0.306	0.0	0.000
MOZ 11	0.0	0.000	0.2	0.067
MOZ 12	1.0	0.303	0.2	0.068

2.2.4. Synthesis of PMMA using bromoform under thermal conditions

The following method describes the synthesis of PMMA under thermal conditions with variable quantities of AIBN and bromoform, as depicted in Scheme 2.4.



Scheme 2.4. Preparation of PMMA using 5 g (50 mmol) MMA with variable but known, quantities of AIBN and concentrations of bromoform in 10 mL THF. The reactions were conducted in a 70 °C oil bath.

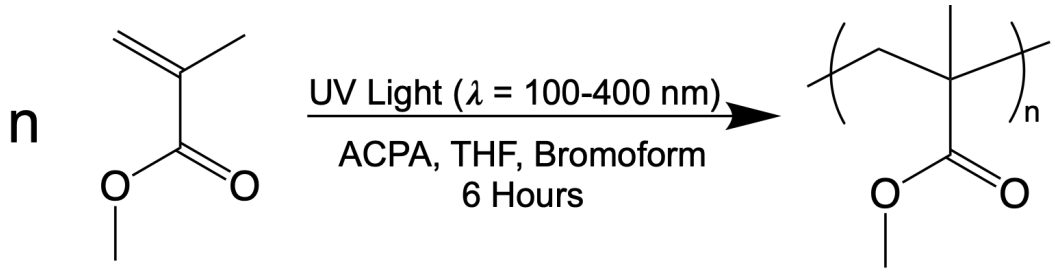
5 g (50 mmol) MMA and AIBN were weighed into a 50 mL round bottom flask containing 10 mL of THF with a variable but known, the concentration of bromoform. The reaction flask was then sealed with a rubber septum containing a magnetic stirring bar. Following this, the mixture was stirred for 30 mins, then degassed 3 times via vacuum and nitrogen cycles. The reaction mixture was sealed under nitrogen and immersed in a 70 °C preheated oil bath. At intervals of 1 h, two samples of 20 μL of the reaction mixture were withdrawn using a pipette for kinetic studies (during this operation a stream of nitrogen was introduced, and ventilation was provided). The two samples were used to calculate monomer conversion and the molar mass of the polymer using ^{1}H NMR and GPC, respectively. As the reaction proceeded the solution became viscous, and after 24 hours, the polymerisation was terminated by unsealing the flask and quenching the flask in ice. The resulting polymer was dissolved in 10 mL THF and added dropwise to stirred cold methanol (200 mL). Excess methanol was decanted, and the polymer was collected by filtration using a Buchner funnel to yield. The solid was then ground into a white powder using a pestle and mortar and then dried overnight on the vacuum pump.

Table 2.3. Preparation of PMMA using 5 g (50 mmol) MMA with variable quantities of bromoform and AIBN (listed below for each experiment) in 10 mL THF. The reactions were conducted at 70 °C for 24 hours, e.g. MMA:bromoform:AIBN = 40:1:0.2

Experimental Code	Molar equivalents of bromoform added	Mass of bromoform added (g)	Molar equivalents of AIBN added	Mass of AIBN added (g)
MOZ 15	0.0	0.000	0.0	0.000
MOZ 16	1.0	0.317	0.0	0.000
MOZ 17	0.0	0.000	0.2	0.043
MOZ 18	1.0	0.316	0.2	0.041
MOZ 19	0.5	0.159	0.2	0.042
MOZ 29	0.1	0.032	0.2	0.040
MOZ 30	0.2	0.063	0.2	0.041
MOZ 31	2.0	0.632	0.2	0.043
MOZ 32	1.0	0.316	0.1	0.021
MOZ 33	1.0	0.317	0.5	0.102
MOZ 34	1.0	0.317	1.0	0.205

2.2.5. Synthesis of PMMA using bromoform under UV conditions

The following method describes the synthesis of PMMA under UV conditions using variable quantities of ACPA and bromoform, as depicted in Scheme 2.5.



Scheme 2.5. Preparation of PMMA under UV conditions using 5 g (50 mmol) MMA with variable but known, quantity of ACPA and concentrations of bromoform in 10 mL THF.

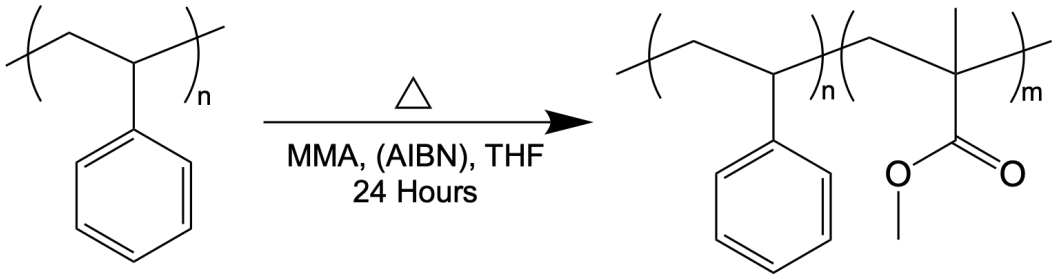
5 g (50 mmol) styrene and ACPA were weighed into a 50 mL round bottom flask containing 10 mL of THF with a variable but known, the concentration of bromoform. The reaction flask was then sealed with a rubber septum containing a magnetic stirring bar. Following this, the mixture was stirred for 30 mins, then degassed 3 times via vacuum and nitrogen cycles. The reaction mixture was sealed under nitrogen and then placed in the aluminium box by balancing on a clear dish. The UV lamp was placed on top of the box, the distance between the flask was roughly 15 cm. The UV lamp was switched on for 6 hours. At intervals of 1 h, two samples of 20 μL of the reaction mixture were withdrawn using a pipette for kinetic studies (during this operation a stream of nitrogen was introduced, and ventilation was provided). The two samples were used to calculate monomer conversion and the molar mass of the polymer using ^{1}H NMR and GPC respectively. The reactions were terminated after 6 hours by unsealing the flask and quenching into ice. The resulting polymer was redissoled in 10 mL THF and added dropwise to stirred cold methanol (200 mL). Excess methanol was decanted and the polymer was collected by filtration using a Buchner funnel to yield a white solid. The solid was then ground into a powder using a pestle and mortar and then dried overnight on the vacuum pump.

Table 2.4. Preparation of PMMA under UV conditions by irradiating the reaction flasks with UV light (λ = 100-400 nm) for 6 hours. The reaction flasks contained 5 g MMA and selected quantities of ACPA and bromoform (listed below for each experiment) in 10 mL THF, e.g. MMA:bromoform:ACPA = 40:1:0.2

Experimental Code	Molar equivalents of bromoform added	Mass of bromoform added (g)	Molar equivalents of ACPA added	Mass of ACPA added (g)
MOZ 20	0.0	0.000	0.0	0.000
MOZ 21	1.0	0.316	0.0	0.000
MOZ 22	0.0	0.000	0.2	0.071
MOZ 23	1.0	0.317	0.2	0.072
MOZ 24	0.1	0.033	0.2	0.069
MOZ 25	0.5	0.157	0.2	0.070
MOZ 26	2.0	0.631	0.2	0.071
MOZ 27	1.0	0.316	0.1	0.035
MOZ 28	1.0	0.316	0.5	0.176
MOZ 35	1.0	0.315	1.0	0.351
MOZ 36	0.2	0.063	0.2	0.072

2.2.6. Synthesis of PS-*b*-PMMA block copolymers using PS as a macroinitiator/ macro-CTA under thermal conditions

The following experimental method describes the synthesis of PS-*b*-PMMA under thermal conditions with and without the addition of AIBN, as depicted in Scheme 2.6.

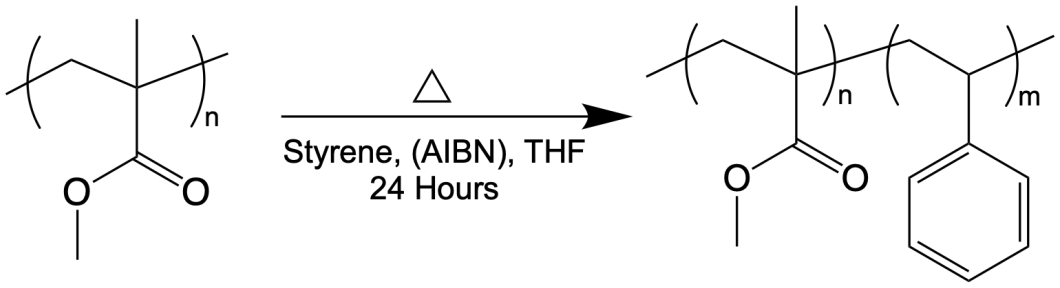


Scheme 2.6. Preparation of PS-*b*-PMMA using 0.502 g PS (prepared from the thermal polymerisation of styrene using 1.0 molar equivalents bromoform and 0.2 molar equivalents AIBN), 0.482 g (0.052 mmol) MMA in 5 mL THF. The reactions were conducted with and without the addition of 0.2 molar equivalentsAIBN in a 70 °C oil bath.

PS prepared from the thermal polymerisation of styrene using 1.0 molar equivalents bromoform and 0.2 molar equivalents AIBN was used as a macroinitiator/macro-CTA for these experiments. A 25 mL round bottom flask was charged with a mixture of 0.482 g (0.052 mmol) MMA and 0.502 g (0.052 mmol) PS in 5 mL THF. The reaction flask was then sealed with a rubber septum containing a magnetic stirring bar. Following this, the mixture was stirred for 30 mins, then degassed via vacuum and nitrogen cycles. The reaction mixture was sealed under nitrogen and immersed in a 70 °C preheated oil bath. At intervals of 1 h, two samples of 20 μL of the reaction mixture were withdrawn using a pipette for kinetic studies (during this operation a stream of nitrogen was introduced, and ventilation was provided). The two samples were used to calculate monomer conversion and the molar mass of the polymer using ^{1}H NMR and GPC, respectively. As the reaction proceeded the solution became viscous, and after 24 hours, the polymerisation was terminated by unsealing the flask and quenching the flask in ice. The resulting polymer was dissolved in 10 mL THF and added dropwise to stirred cold methanol (200 mL). Excess methanol was removed using a rotary evaporator and stored below 0 °C overnight. The polymer was collected by filtration using a Buchner funnel. The solid was then ground into a powder using a pestle and mortar, and then dried overnight on the vacuum pump. The experiment was then repeated with the addition of 1.69 mg (0.01 mmol) AIBN, to identify if PS behaved as a macro-CTA/macromonomer.

2.2.7. Synthesis of PMMA-*b*-PS block copolymers using PMMA as a macro-initiator/ macro-CTA under thermal conditions

The following method describes the synthesis of PMMA-*b*-PS under thermal conditions with and without the addition of as depicted in Scheme 2.7.



Scheme 2.7. Preparation of PMMA-*b*-PS using PMMA (prepared from the thermal polymerisation of MMA using 1.0 molar equivalents bromoform and 0.2 molar equivalents AIBN) and styrene in 5 mL THF. The reactions were conducted with and without the addition of 0.2 molar equivalentsAIBN in a 70 °C oil bath.

PMMA prepared from the thermal polymerisation of MMA using 1.0 molar equivalents bromoform and 0.2 molar equivalents AIBN was used as a macroinitiator/macro-CTA, for these experiments. A 25 mL round bottom flask was charged with a mixture of styrene, and PMMA in 5 mL THF. The flask was sealed with a rubber septum containing a magnetic stirring bar. The reaction mixture was stirred for 30 mins, then degassed via vacuum and nitrogen cycles. The reaction mixture was sealed under nitrogen and immersed in a 70 °C preheated oil bath. At intervals of 1 h, two samples of 20 μL of the reaction mixture were withdrawn using a pipette for kinetic studies (during this operation a stream of nitrogen was introduced, and ventilation was provided). The two samples were used to calculate monomer conversion and the molar mass of the polymer using ^{1}H NMR and GPC, respectively. As the reaction proceeded the solution became viscous, and after 24 hours, the polymerisation was terminated by unsealing the flask and quenching the flask in ice. The resulting polymer was dissolved in 10 mL THF and added dropwise to stirred cold methanol (200 mL). Excess methanol was removed using a rotary evaporator and stored below 0 °C overnight. The polymer was collected by filtration using a Buchner funnel. The solid was then ground into a powder using a pestle and mortar and then dried overnight on the vacuum pump. The reaction was repeated with the addition of 6.8 mg (0.004 mmol) AIBN, to identify if PMMA behaved as a macro-CTA/macromonomer.

Table 2.5. Preparation of PMMA-*b*-PS block copolymers using PMMA (prepared using 1 molar equivalents bromoform and 0.2 molar equivalents AIBN under thermal conditions) as a macro-initiator/macro-CTA with variable quantities of styrene in 5 mL THF. The reactions were conducted at 70 °C for 24 hours.

Experimental Code	Target number of MMA units per 100 units	Mass of PMMA Added (g)	Target number of styrene per 100 units	Mass of styrene added (g)
MOZ 39A	10	0.102	90	0.936
MOZ 39B	25	0.251	75	0.781
MOZ 39C	40	0.404	60	0.621
MOZ 39	50	0.501	50	0.522
MOZ 39D	60	0.603	40	0.410
MOZ 39E	75	0.750	25	0.259
MOZ 39F	90	0.901	10	0.105
***MOZ 40**	50	0.502	50	0.520

*MOZ 40 contained 6.8 mg (0.004 mmol) of AIBN.

2.3. CHARACTERISATION METHODS

The following section details the instruments and methods used for kinetic studies and the characterisation of the polymers physical and thermal properties. For kinetic studies, monomer conversion and molar mass progression during the polymerisation were monitored.

2.3.1. Nuclear Magnetic Resonance Spectroscopy

Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) was used to calculate monomer conversion. The technique was used to compare the vinyl protons from the monomer to the polymer protons. As the polymerisation reaction proceeds, the vinyl protons start to decrease in terms of resonance signal intensity, and the intensity of the polymer protons resonance signals increases. The results from the NMR spectrum can then be used to derive an equation which compares the vinylic protons with the polymer protons.

For the preparation of PS, the resonance signals of the vinyl protons on the monomer is compared to the resonance signals of the protons on the phenyl ring for both monomer and polymer. As the polymerisation proceeds the intensity of the resonance signals of the protons for the monomer decreases and the intensity of the signals for the protons on the polymer increases. Equation 2.1 outlines an equation which relates the integration values for vinyl peaks on the monomer to the extent of reaction, *x*. This can be rearranged and converted to an equation in terms of monomer conversion (Equation 2.2).

$$\frac{\text{Integration of vinyl peaks on monomer}}{\text{Integration of protons from benzene ring on polymer+monomer}} = \frac{2(1-x)}{5x+5(1-x)} \qquad \text{(Equation 2.1)}$$

$$\text{Monomer conversion (\%)} = \frac{\left[2-5\,\frac{\text{(Integration for monomer peaks)}}{\text{(Total Intergration for 56olymer peaks)}}\right]}{2} \times 100 \qquad \text{(Equation 2.2)}$$

For MMA the methyl groups remain in both monomer and polymer. Therefore, the monomer conversion can be estimated by comparing the intensity of the resonance signals of the vinyl protons to the integration of methyl protons on the polymer. Equation 2.3 can be used to calculate the monomer conversion for the preparation of PMMA.

$$\text{Monomer conversion (\%)} = \frac{\left[2-3\,\frac{\text{(Integration area for monomer peaks)}}{\text{(Total Intergration for 56olymer peaks)}}\right]}{2} \times 100 \qquad \text{(Equation 2.3)}$$

The NMR measurements preformed in this project used a 300 MHz Bruker Avance spectrometer with TMS as an internal reference. For sample preparation approximately 5 mg of the polymer reaction mixture was dissolved in 1 mL of deuterated solvent (chloroform or acetone).

2.3.2. Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) also known as Size Exclusion Chromatography (SEC) is a technique which is widely used to obtain molar mass data of a polymer. The GPC column makes use of a stagnant solvent which is present in porous beads whose structure is cross-linked to form a gel and a flowing solution as the mobile phase. The mobile phase flows between the semisolid polymer materials and elutes in and out the pores of the material. The large molecules, which occupy the greatest effective volume in solution, are excluded from the smaller pore sizes in the gel and bypass through the larger channels between the gel particles. This results in them being eluted first from the column. As the molecular sizes of the polymer decreases, there's an increasing probability the molecules diffuse into the smaller pores and channels in the gel, which slows their time of passage through the column by providing a potentially longer path length before being eluted.[94]

In this study, GPC has been used to measure the polymer number average molecular weight (M_n), weight average molecular weight (M_w) and the dispersity ($Đ$). To obtain these values an Agilent infinity 1260 GPC consisting of two PL gel mixed C columns, consisting of particles with size of 5 µm and a length of 300 x 7.5 mm with an MW Range of 200-2,000,000 g/mol as well as a guard column was used. The mobile phase consisted of degassed THF containing 0.02 % triethylamine, at a flow rate of 1 mL min^{-1} at 40 °C and toluene a flow marker. The calibration curves were produced using either near monodispersed PMMA (M_p range = 690 to 1,944,000 g/mol) or monodispersed PS (M_p

range = 158 to 30,220,00 g/mol). Samples were prepared by dissolving roughly 5 mg of the polymer reaction mixture in 1 mL of THF eluent and passing through a 0.45 µm Millipore syringe filter. Agilent GPC software (version 2.1.9.34851) provided by Agilent technologies was used to analyse the data. PMMA and PS-*b*-PMMA prepared were analysed using the calibration curves for monodispersed PMMA. The PS and PMMA-*b*-PS were analysed using the calibration curves for monodispersed PS.

2.3.3. Fourier Transform infrared Spectroscopy

Infrared spectroscopy can be used to characterise long-chain polymers because the infrared active groups present along the chain, absorb as if each was a localised group in a simple molecule. Identification of polymer samples can be made by making use of the 'fingerprint' region, where it is least likely for one polymer to exhibit the same spectrum as another. In polymer chemistry, Fourier transform infrared (FTIR) spectroscopy has been used successfully to identify polymer end groups and hydrogen bonding in polymer bends.[95]

FTIR spectroscopy was acquired at room temperature using a Thermo Nicolet 380 FTIR instrument. Precipitated polymers were placed directly onto the diamond plate and 64 scans of attenuated total reflectance (ATR) were used. A resolution of 4 cm^{-1} was adopted over the range 400 cm^{-1} to 4000 cm^{-1}.

2.3.4. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is widely used to determine the crystallinity of semi-crystalline polymers and the glass transition temperature (T_g). Amorphous polymers such as PS and PMMA are hard and brittle at temperatures below T_g. Heating the polymer to temperatures above T_g, they become more mobile. When approaching the glass transition temperatures from high temperatures the molecules or segments of molecules increasingly impede one another's movement and the viscosity rises rapidly until the material finally solidifies.[96]

DSC experiments were performed using Mettler Toledo instrument. For sample preparation, 7-10 mg of the polymer was loaded into a DSC pan (obtained from Toledo) with a pierced lid. The method used consisted of three heat-cool cycles with temperature holding. The initial heat cycle involved heating the sample from 25 °C to 150 °C at 10 °C min^{-1}. The temperature was then held at 150 °C for 5 mins. The samples were then cooled from 150 °C to 25 °C at -10 °C min^{-1} and then held at the new temperature for a further 5 min. Finally, the sample was heated from 25 °C to 150 °C at 10 °C min^{-1}. The DSC curves were analysed

using Mettler's STAR software. The glass transition temperature was determined from the last heating cycle.

2.3.5. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a technique where the mass of a substance is monitored as the sample is subjected to a controlled temperature program. TGA consists of a ceramic sample pan that is supported by a precision balance. The pan resides in a furnace and is heated during the experiment. When TGA is conducted in an inert atmosphere this is called pyrolysis, this technique is used to investigate the degradation of polymer chains.[97]

TGA was conducted using a Pyris 1 thermogravimetric analyser. 10 mg of the polymer samples was loaded onto a ceramic TGA pan and loaded onto the instrument. TGA curves were obtained under N_2 atmosphere at a thermal decomposition temperature ranging from 30 °C to 500 °C at a rate of 10 °C/min.

2.3.6. Diffusion Ordered Spectroscopy

Diffusion ordered NMR spectroscopy (DOSY NMR) is a two-dimensional NMR technique in which the signal decays exponentially due to the self-diffusion behaviour of individual molecules. This leads to two dimensions: the first dimension (F_2) accounts for the conventional chemical shift and the second one (F_1) for self-diffusion coefficients (D). The diffusion coefficient is related to the properties of an individual molecule such as size, mass and charge as well as its surrounding environments, such as solution, temperature and aggregation states. Thus, each component of a mixture can be pseudo-separated, based on its diffusion coefficient on the diffusion dimension.[98] Chen *et al*.[87] was the first researchers to use DOSY in polymer chemistry. In their research, DOSY was used to characterise the molecular weight distributions of poly(ethylene oxide) in D_2O. Following this Jerschow *et al*.[99] used DOSY to study homopolymer mixtures for industrial applications. Recently, block copolymers have been characterised by DOSY experiments to interpret the structure of target polymers.[100,101] The results showed DOSY can be a powerful technique to detect traces of impurities, unreacted monomers, or residual homopolymers.

DOSY measurements were performed at 298 K on a Bruker Avance AQS600 NMR spectrometer operating at 300 MHz. The DOSY spectrum was acquired with ledbgp2s pulse program from Bruker topspin software. The gradient strength was logarithmically incremented in 10 steps from 2 % up to 80 % of the maximum gradient strength. All measurements were performed with a compromise diffusion delay of 200 ms to keep the relaxation contribution to the signal attenuation constant for all samples. The gradient pulse

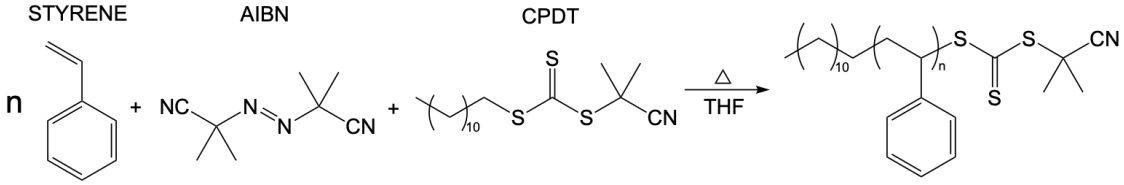
length was 5 ms to ensure full signal attenuation. The 2D DOSY maps were processed and obtained using DOSY toolbox software by Bruker. For sample preparation 50 mg of the polymer was dissolved in 1 mL deuterated chloroform containing 1 drop of TMS .

CHAPTER 3

PREPARATION OF POLYSTYRENE UNDER THERMAL AND ULTRAVIOLET CONDITIONS

3.1. RAFT POLYMERISATION OF STYRENE

The preliminary reaction conducted was the production of PS using RAFT polymerisation. For this polymerisation cyano-2-propyl dodecyl trithiocarbonate (CPDT) was used as the CTA, shown in Scheme 3.1. Literature has reported that CPDT is an efficient CTA, which provides excellent control over the molar mass dispersity for the polymerisation of styrene.[102] RAFT polymerisation was used to understand the technique involved when conducting a radical polymerisation, and the results obtained were desmed to be useful when comparing to the bromoform-mediated polymerisation.



Scheme 3.1. RAFT polymerisation of styrene using CPDT as a CTA and AIBN as the thermal initiator, outlining the structure of the polymer end groups.

Molar mass and monomer conversion data are shown in Table 3.1. After 140 hours, conversion of 98 % was achieved. The molar mass data was obtained from GPC against monodispersed PS standards. The molar mass data shows RAFT polymerisation for styrene was successful as a small difference was observed between the observed M_n to the target degree of polymerisation. Table 3.1 shows the polymers produced have low dispersity (<1.10) which is characteristic for RAFT polymerisation.

Table 3.1. Molar mass data for the RAFT polymerisation of 2 g (19.2 mmol) styrene using 1 molar equivalentsCPDT as a CTA and 0.2 molar equivalentsAIBN in 5 mL THF at 70 °C.

Code	Molar equivalents of CTA added [(a)]	Theoretical M_n (g/mol) [(a)]	Monomer conversion (%) [(b)]	Actual M_n (g/mol) [©]	$Đ$ [©]	k_{app} (h^{-1}) [(d)]
MOZ 01	1.0	4520	98	3,600	1.10	0.013

(a) Target degree of polymerisation DP = 40

(b) Monomer conversion determined by ^{1}H NMR spectroscopy

(c) M_n and $Đ$ determined by GPC [polystyrene standards]

(d) The apparent rate constant (measured by ^{1}H NMR spectroscopy)

3.1.1. Polymerisation kinetics for the RAFT polymerisation of styrene

The kinetics for the reactions were followed by GPC and ^{1}H NMR spectroscopy, with samples taken at various times for a duration of 150 hours. The reaction was stopped after 150 hours, due to solvent evaporation which resulted in the reaction medium to increase in viscosity and therefore the stirring to stop. The plot of monomer conversion *versus* time is shown in Figure 3.1 and molar mass *versus* time in Figure 3.2. The plots show a linear progression for monomer conversion and molar mass across time. This is not expected to be linear, due to the monomer consumption through the polymerisation changing in radical polymerisation.

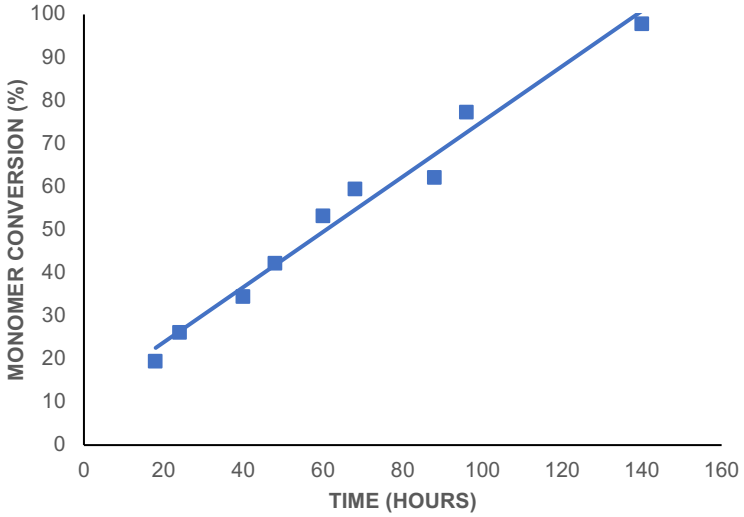


Figure 3.1. Monomer conversion *versus* time for the RAFT polymerisation of styrene with a target degree of polymerisation of 40 using 17 mg (0.5 mmol) CPDT and 15 mg (0.1 mmol) AIBN in 5 mL THF at 70 °C for 140 hours.

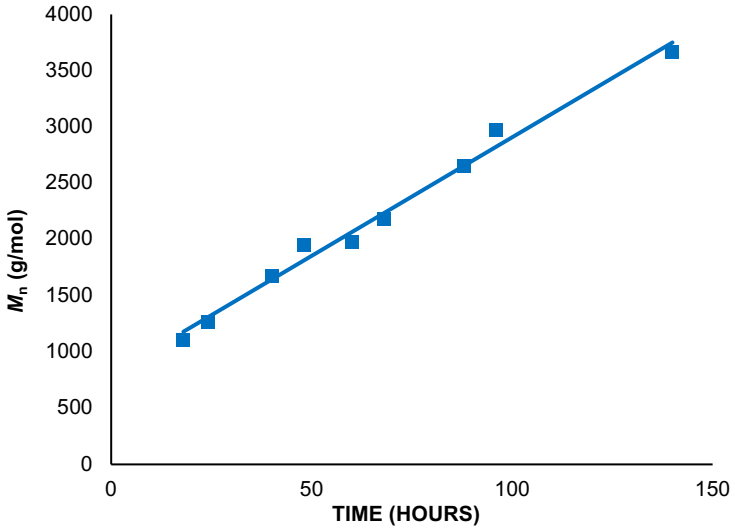


Figure 3.2. Molar mass (M_n) *versus* time for the RAFT polymerisation of styrene with a target degree of polymerisation of 40 using 17 mg (0.5 mmol) CPDT and 15 mg (0.1 mmol) AIBN in 5 mL THF at 70 °C for 140 hours.

Molar mass and dispersity *versus* monomer conversion are presented in Figure 3.3. The figure shows a linear progression of molar mass against monomer conversion, the dispersity of the polymer chains remained less than 1.10 throughout the reaction.

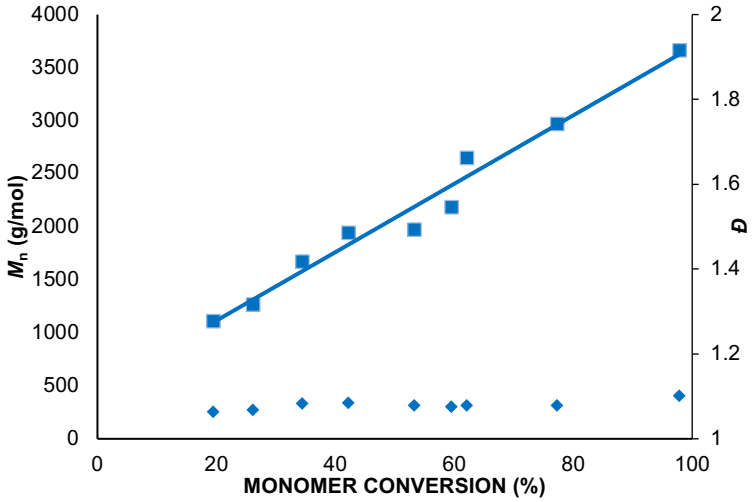


Figure 3.3. Molar mass (M_n, denoted by ■) and Dispersity (*Đ,* denoted by ◆) *versus* monomer conversion for the RAFT polymerisation of styrene with a target degree of polymerisation of 40 using 17 mg (0.5 mmol) CPDT and 15 mg (0.1 mmol) AIBN in 5 mL THF at 70 °C for 140 hours.

The semi-logarithmic plot, showing the first order dependence on monomer concentration, is given in Figure 3.4. Initially, a linear progression is observed, indicating a constant radical concentration with an apparent rate constant of 0.013 h^{-1}. However, after 88 hours, a faster polymerisation regime is observed with an apparent rate constant of 0.0538 h^{-1}. This deviation is characteristic for the Trommsdorff-Norrish effect.[103] Literature has suggested the differences in kinetics can arise due to the localised increase viscosity of the polymerising system that slows termination reactions. The removal of reaction obstacles therefore causes a rapid increase in overall rate of reaction.

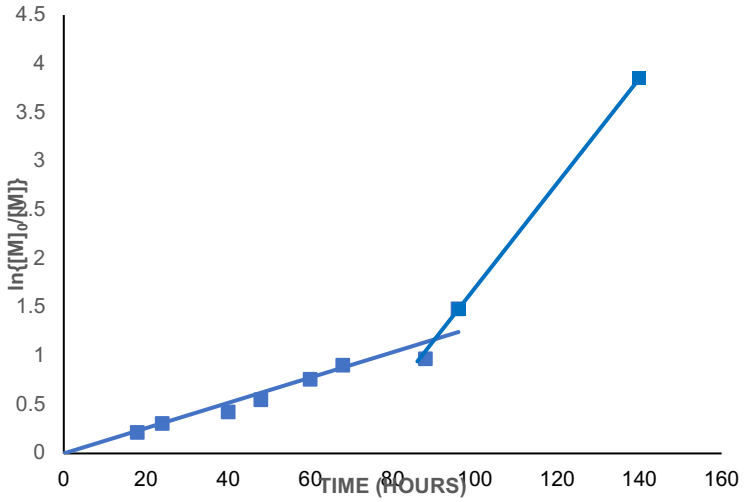


Figure 3.4. Semi-logarithmic plot for the RAFT polymerisation of styrene with a target degree of polymerisation of 40 using 17 mg (0.5 mmol) CPDT and 15 mg (0.1 mmol) AIBN in 5 mL THF at 70 °C for 140 hours.

The GPC traces for the RAFT polymerisation of styrene are shown in Figure 3.5, showing unimodal molar mass distributions for the reaction. Figure 3.5 shows a clear change in retention time for each GPC trace which implies a change in the polymer chain length. The GPC traces have narrow distributions which is characteristic for RAFT polymerisation.

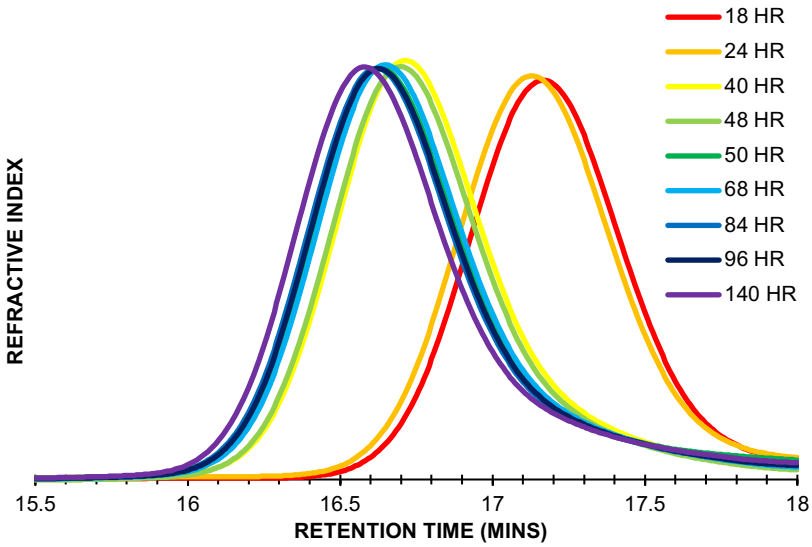
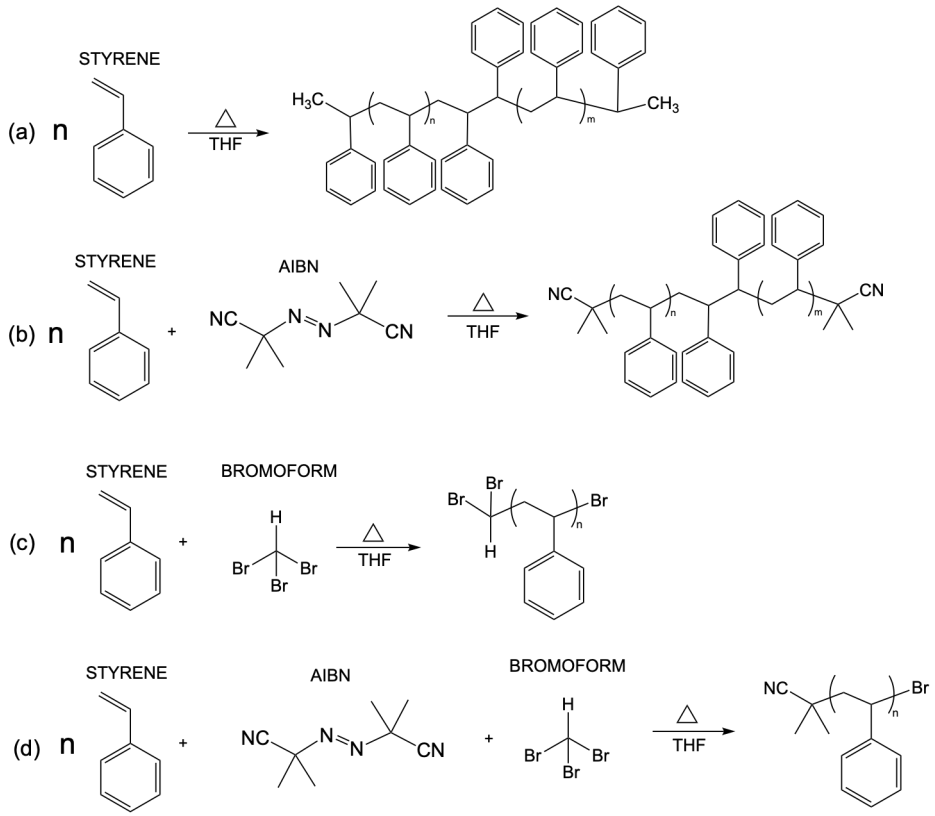


Figure 3.5. GPC traces for the RAFT polymerisation of styrene with a target degree of polymerisation of 40 using 17 mg (0.5 mmol) CPDT and 15 mg (0.1 mmol) AIBN in 5 mL THF at 70 °C across 140 hours.

3.2. THE EFFECT BROMOFORM HAS ON THE RADICAL POLYMERISATION OF STYRENE UNDER THERMAL CONDITIONS

Following the preliminary RAFT polymerisation, a variety of experiments were designed to identify the role of bromoform in a series of radical polymerisation of styrene. The reactions conducted included the following: self-initiated thermal polymerisation of styrene at 70 °C, a conventional radical polymerisation using AIBN, a reaction where bromoform is used as a possible thermal initiator and a reaction where bromoform is added to a conventional radical polymerisation. The reaction scheme for these experiments are shown in Scheme 3.2. The structure of the end groups have been outlined from the following assumptions: (a) The self-initiated polymerisation of styrene proceeds via Flory's[104] and Mayo's[105] mechanism for the spontaneous generation of radicals from styrene, (b) the reaction proceeds via termination by combination (for convenience purpose), (c) bromoform behaves as a thermal initiator by the thermal decomposition of bromoform, and both radicals can behave as the initiating radical and (d) bromoform behaves as a CTA which produces polymers with bromine end groups.



Scheme 3.2. Synthesis of PS via self-initiated polymerisation (a), using AIBN as a thermal initiator (b), using bromoform as a thermal initiator (c) and using bromoform as a CTA with AIBN (s). The reactions were conducted in 10 mL THF at 70 °C for 72 hours. For simplicity only major products are shown.

The molar mass and monomer conversion data for these experiments are shown in Table 3.2. Overall, high monomer conversion (> 90 %) was achieved for the reactions where AIBN was used with bromoform under thermal conditions (70 °C). The ^{1}H NMR spectra showed using bromoform alone does not behave as a thermal initiator at 70 °C, as conversion was less than 5 %. The results showed under the current conditions, styrene doesn't undergo self-initiated polymerisation at 70 °C in THF. Literature reported at elevated temperatures (100-200 °C) styrene can undergo self-initiated thermal polymerisation via the generation of a radical, which is capable of polymerising with styrene.[106] The results in Table 3.2 suggests the presence of bromoform has a major effect on the observed molar mass of the polymers produced. Increasing the concentration of bromoform resulted in a low molar mass polymers being formed. When comparing the obtained M_n to the target degree of polymerisation a significant difference was observed. The molar mass data shows that the polymer produced using bromoform have a lower dispersity compared to the polymers produced using a conventional radical polymerisation. However, the observed effect is not clear due to only two different molar equivalents of bromoform being used.

Table 3.2. Molar mass data for the polymerisation of 5 g (48 mmol) styrene using 0.2 molar equivalentsAIBN with 0.5 and 1 molar equivalents bromoform in 10 mL THF. The reactions were conducted at 70 °C for 72 hours.

Code	Molar equivalents of bromoform added [(a)]	Molar equivalents of AIBN added	Theoretical M_n (g/mol)	Monomer conversion (%) [(b)]	Observed M_n (g/mol) [©]	$Đ$ [©]	k_{app} (h^{-1}) [(d)]
MOZ 05	0	0	-	3	-	-	-
MOZ 06	1.0	0	-	5	-	-	-
MOZ 07	0	0.2	-	99	34,000	1.79	0.033
MOZ 13	0.5	0.2	8,320	92	13,000	1.59	0.085
MOZ 14	1.0	0.2	4,160	94	9,600	1.34	0.096

(a) Molar equivalents of styrene = 40, theoretical M_n based on assuming bromoform behaves as a CTA similar to RAFT polymerisation.

(b) Monomer conversion determined by ^{1}H NMR spectroscopy

(c) M_n and $Đ$ determined by GPC (polystyrene standards)

(d) The apparent rate constant (measured by ^{1}H NMR spectroscopy)

(e) Experiments were carried out once, due to limited time constraints.

The kinetics for the experiments were followed by GPC and ^{1}H NMR spectroscopy, samples were taken at various times for the duration of 72 hours. The reactions were stopped after 80 hours, due to solvent evaporation and simultaneous polymerisation which resulted in an increase in reaction medium viscosity and therefore the stirring to stop. The plots of monomer conversion *versus* time are shown in Figure 3.6 and molar mass *versus* time in Figure 3.7. For all of the reactions conducted, no inhibition period was observed. Figure 3.6 shows that the addition of bromoform results in high conversion being reached earlier compared to the conventional radical polymerisation. For a radical polymerisation, we would expect the reaction to reach high conversions significantly quicker compared to the other two reactions. Which may imply the reaction was not conducted successfully. The graph shows a marginal change to monomer conversion, when the concentration is doubled. Figure 3.7 shows the addition of bromoform results in the formation of low molar mass polymers compared to the conventional radical polymerisation. The graph shows a small decrease in observed molar mass when the concentration of bromoform is doubled.

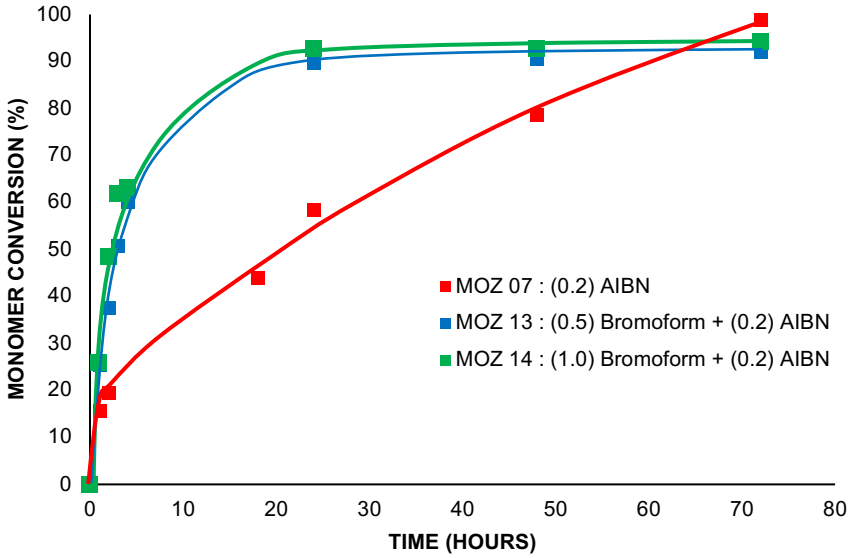


Figure 3.6. Monomer conversion *versus* time for the radical polymerisation of styrene using 0.2 molar equivalents AIBN and 0.5 and 1.0 molar equivalents bromoform. The reactions were conducted in 10 mL THF at 70 °C.

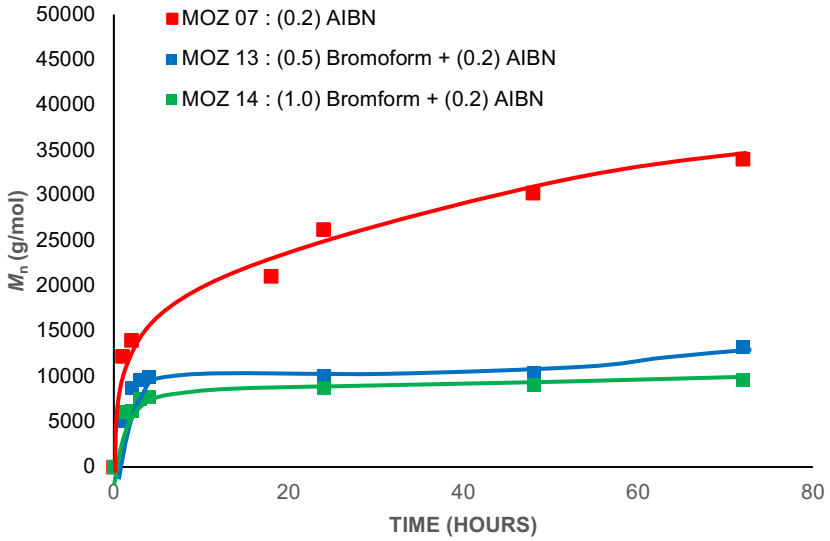


Figure 3.7. Molar mass (M_n) *versus* time for the radical polymerisation of styrene using 0.2 molar equivalents AIBN and 0.5 and 1.0 molar equivalents bromoform. The reactions were conducted in in 10 mL THF at 70 °C.

Figure 3.8 presents the molar mass and dispersity *versus* monomer conversion. The graph suggests a radical mechanism, where 'high' M_n polymers are achieved early in the reaction. From the two experiments conducted using bromoform, the addition of bromoform is hindering the production of high molar mass polymers and increasing the concentration of bromoform produces polymers of low molar mass and low dispersity.

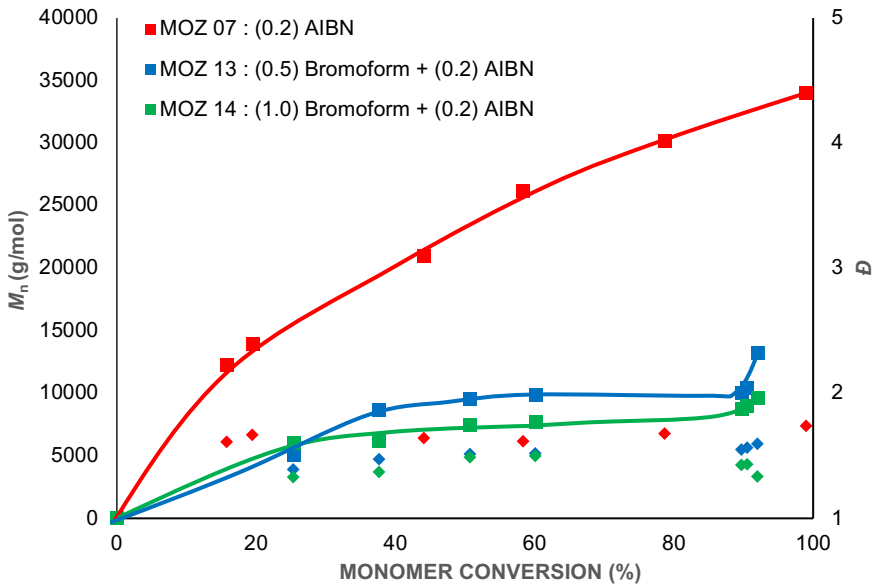


Figure 3.8. Molar mass (M_n, denoted by ■) and Dispersity ($Đ$, denoted by ◆) *versus* monomer conversion for the radical polymerisation of styrene using 0.2 molar equivalents AIBN and 0.5 and 1.0 molar equivalents bromoform. The reactions were conducted in in 10 mL THF at 70 °C.

The semi-logarithmic plots, showing the first order dependence on monomer concentration, is given in Figure 3.9. The experiments initially show two-step linear progression for all reactions, indicating a change in radical concentration. A larger apparent rate constant is observed for the polymerisations using bromoform. The polymerisation using 0.5 and 1.0 molar equivalents bromoform had apparent rate constants of 0.085 h^{-1} and 0.096 h^{-1}, respectively. This may suggest the addition of bromoform, releases more radicals into the system, compared to the conventional radical polymerisation, which had an apparent rate constant of 0.033 h^{-1}. However, a second polymerisation regime is observed for all reactions. For the reaction conducted using bromoform, a slower regime is observed with a smaller apparent rate constant. This could suggest a termination step/reaction or slower polymerisation rate due to poor mixing due to an increase in viscosity to the reaction medium. This is based on the data points following the two data points precisely. For the conventional radical polymerisation, a second faster regime is noted, this however, is reliant on one data point, and therefore might not be accurate. If repeats were conducted on these experiments, the reaction may have shown a linear or multi progression instead of what has been identified.

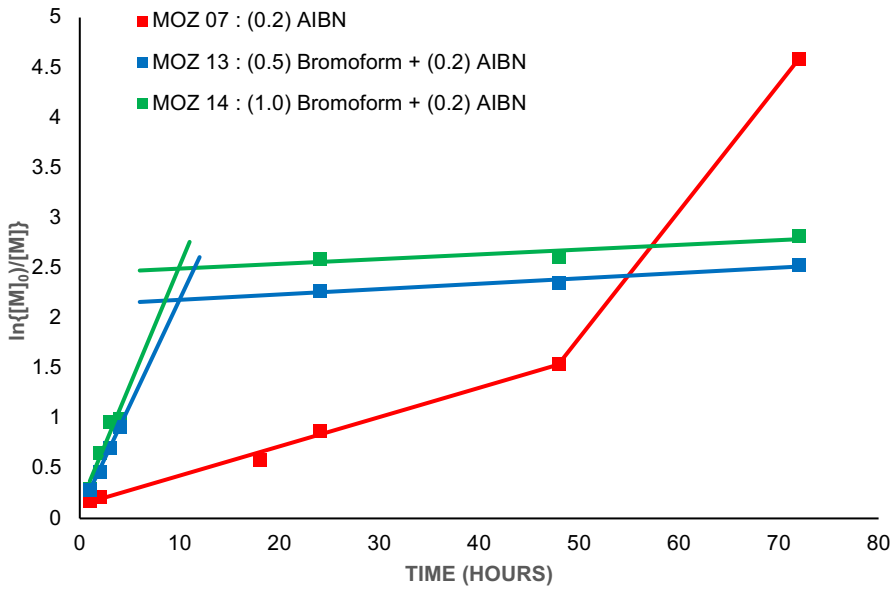


Figure 3.9. Semi-logarithmic plots for the radical polymerisation of styrene using 40 mg (0.24 mmol) AIBN and variable quantities of bromoform. The reactions were conducted in 10 mL THF at 70 °C.

3.2.1. Characterisation of PS prepared using bromoform under thermal conditions

This section goes over the results obtained from the characterisation of the polymers produced from the conventional radical polymerisation and the polymerisation using bromoform. The characterisation techniques include the following: FTIR, DSC and NMR.

FTIR spectroscopy was performed on the precipitated polymers to identify functional groups present in the final polymer. The resulting spectrum for the precipitated polymers is shown in Figure 3.10. The FTIR spectrum contains bands at 695, 1493 and 1600 cm^{-1} are assigned to the stretching of the monosubstituted benzene ring. The spectrum contains a series of C-H vibrations and stretches around at 2900 and 3000 cm^{-1}, which are characteristic to the methylene group and C-H stretch on PS. When comparing all three spectra, no difference is observed. The spectrum does not give any information on the structure of the end groups. From the bromoform-mediated polymerisation, it was assumed the production of a C-Br bond, in the IR spectrum this should be observed as a vibration in the region 500-800 cm^{-1}.[107] This vibration may not be visible due to only relatively small number of C-Br bonds being present in a long polymer chain.

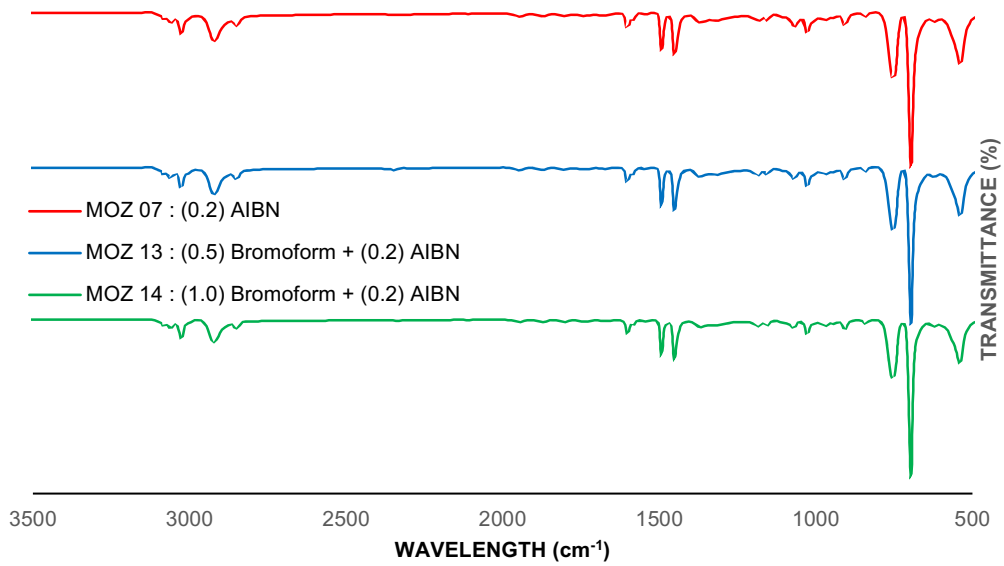


Figure 3.10. FTIR spectrum for the precipitated polymer produced from the radical polymerisation of styrene, using 0.2 molar equivalents AIBN and variable concentration of (0, 0.5, 1 molar equivalents) bromoform. The reactions were conducted in 10 mL THF at 70 °C.

Figure 3.11 shows the DSC thermogram for the polymers produced from the conventional radical polymerisation and the polymers produced from the bromoform-mediated polymerisation. The thermogram shows the presence of one transition centred around 95 °C, which is characteristic of PS homopolymer. The difference between each polymer produced is marginal, which may suggest the difference is due to branching. This could indicate the addition of bromoform results in poymeres being produced with less branching and slightly higher T_g.

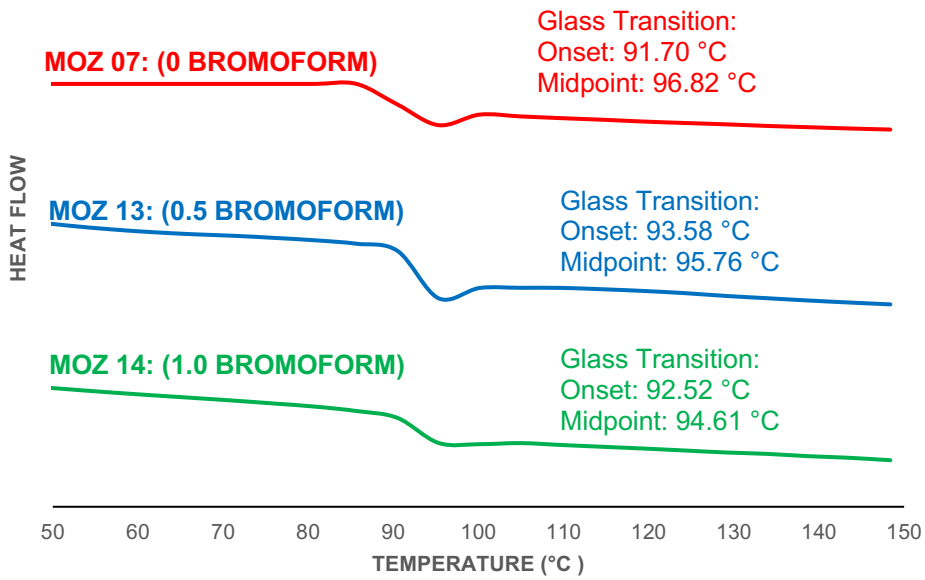


Figure 3.11. Differential scanning calorimetry (DSC) thermogram for the precipitated polymer produced from the radical polymerisation of styrene, using 0.2 molar equivalents AIBN and variable concentration of (0, 0.5, 1 molar equivalents) bromoform. The reactions were conducted in in 10 mL THF at 70 °C.

Figure 3.12 outlines the ^{1}H NMR spectrum for the precipitated polymers from conventional radical polymerisation and the bromoform-mediated polymerisation. The spectrum for all the products consists of 4 broad resonance signals. This includes two resonance signals in the region of 7.56 ppm and 6.25 ppm which are characteristic of benzyl protons and the resonance signals around 2.23 ppm represents methylene protons characteristic for PS. A small signal is visible around 3.55 ppm, for the polymers prepared using 0.5 and 1.0 molar equivalents bromoform. This was found to be from residual THF in the final polymer.

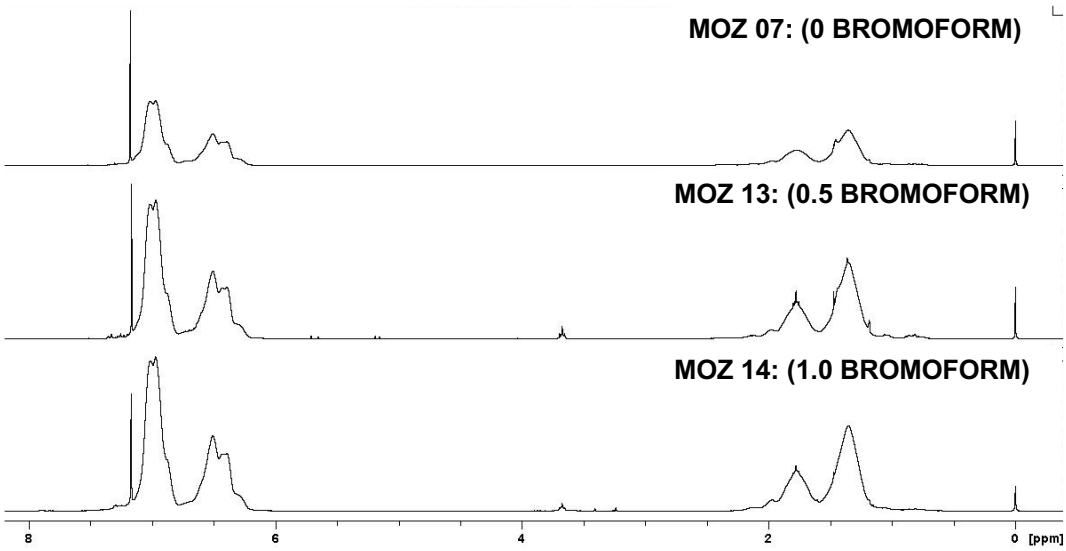
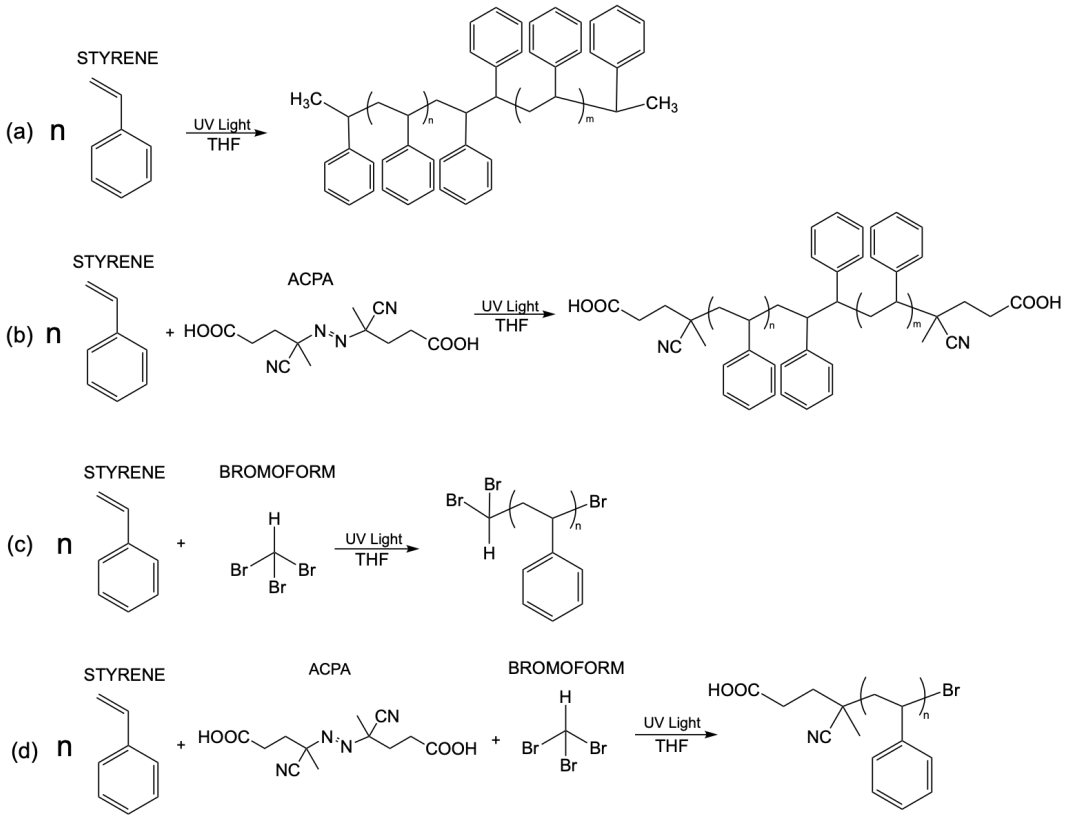


Figure 3.12. ^{1}H NMR spectrum (300 MHz) for the precipitated polymer produced from the radical polymerisation of styrene under thermal conditions, using 0.2 molar equivalents AIBN and (0, 0.5, 1 molar equivalents) bromoform.

3.3. THE EFFECT BROMOFORM HAS ON THE PHOTOPOLYMERISATION OF STYRENE

Following the results from the thermal polymerisation of styrene, the reactions were repeated under UV light. The reactions conducted included the following: a self-initiated polymerisation of styrene under UV light, a conventional radical polymerisation using ACPA, a reaction where bromoform is used as a photoinitiator and a reaction where bromoform is added to a conventional radical polymerisation. The reaction scheme for these experiments have been outlined in Scheme 3.3. The structure of the end groups have been outlined from the following assumptions: (a) The initiating radical for the self-initiated polymerisation of styrene was produced via Flory's[104] and Mayo's[105] mechanism for the spontaneous generation of radicals from styrene, (b) the reaction proceeds via termination by combination (for convenience purpose), (c) bromoform behaves as a photoinitiator by the photolysis of bromoform, where both radicals can behave as initiating radical and (d) bromoform behaves as a CTA which produces polymers with bromine end groups.



Scheme 3.3. Synthesis of PS via self-initiated polymerisation (a), using ACPA as a photo-initiator (b), using bromoform as a photoinitiator (c) and bromoform as a CTA with ACPA (d). Reactions were conducted in 10 mL THF under UV light (λ= 100-400 nm) for 6 hours. For simplicity only major products are shown.

The molar mass and monomer conversion data for these experiments are shown in Table 3.3. Results from the negative control showed styrene doesn't undergo self-initiated polymerisation under UV light in THF. The results show bromoform does not behave as a photoinitiator for the polymerisation of styrene under UV light. This result counters Millers' suggestion for bromoform behaving as a photoinitiator.[2] The results for the conventional radical polymerisation using ACPA, show after 6 hours only 36 % being achieved, which may suggest ACPA is not a suitable photoinitiator, under the current conditions. Table 3.3 shows the addition of bromoform to the conventional radical polymerisation has a significant effect on the achieved conversion after 6 hours and results in the production of low molar mass polymer. This agrees with Thananukul *et.al.*[1] research, which suggested bromoform behaves as a CTA for the photopolymerisation of acrylamides under aqueous systems. The molar mass data shows the polymers produced using the highest concentration of bromoform produced polymers which were closer to the target molar mass. This may not be accurate due to the reactions not reaching high conversions (>90 %).

Table 3.3. Molar mass data for the polymerisation of 5 g (48 mmol) styrene using 0.2 molar equivalents ACPA with 0.5 and 1 molar equivalents bromoform. Reactions were conducted in 10 mL THF under UV light (λ= 100-400 nm) for 6 hours.

Code	Molar equivalents of bromoform added [(a)]	Molar equivalents of ACPA added [(a)]	Theoretical M_n (g/mol) [(a)]	Monomer conversion (%) [(b)]	Observed M_n (g/mol) [©]	$Đ$ [©]	k_{app} (h^{-1}) [(d)]
MOZ 09	0	0	-	3	-	-	-
MOZ 10	1.0	0	-	2	-	-	-
MOZ 11	0	0.2	-	36	7,500	1.46	0.233
MOZ 08	0.5	0.2	8,320	15	5,600	1.43	0.052
MOZ 12	1.0	0.2	4,160	14	4,400	1.61	0.042

(a) Molar equivalents of styrene = 40, theoretical M_n based on assuming bromoform behaves as a CTA similar to RAFT polymerisation

(b) Monomer conversion determined by ^{1}H NMR spectroscopy

(c) M_n and $Đ$ determined by GPC (polystyrene standards)

(d) The apparent rate constant (measured by ^{1}H NMR spectroscopy

(e) Experiments were carried out once, due to limited time constraints

The kinetics for the reactions were followed by GPC and ^{1}H NMR spectroscopy, by taking samples every hour. The reactions were stopped after 6 hours, due to laboratory working hours. As a consequence, the UV light was not irradiated on the reaction flask for more than 6 hours, therefore it was difficult to achieve high conversion. The plots for monomer conversion *versus* time are shown in Figure 3.13 and molar mass *versus* time in Figure 3.14. For all reactions, no inhibition period was observed. Figure 3.13 shows for the conventional radical polymerisation, the reaction reached higher conversions compared to the reactions where bromoform was used. Between the two bromoform concentration used, only a small difference was observed for monomer conversion progression. Figure 3.14 shows the addition of bromoform results in low molar mass polymers being formed and increasing the concentration results in polymers being produced closer to the target molar mass.

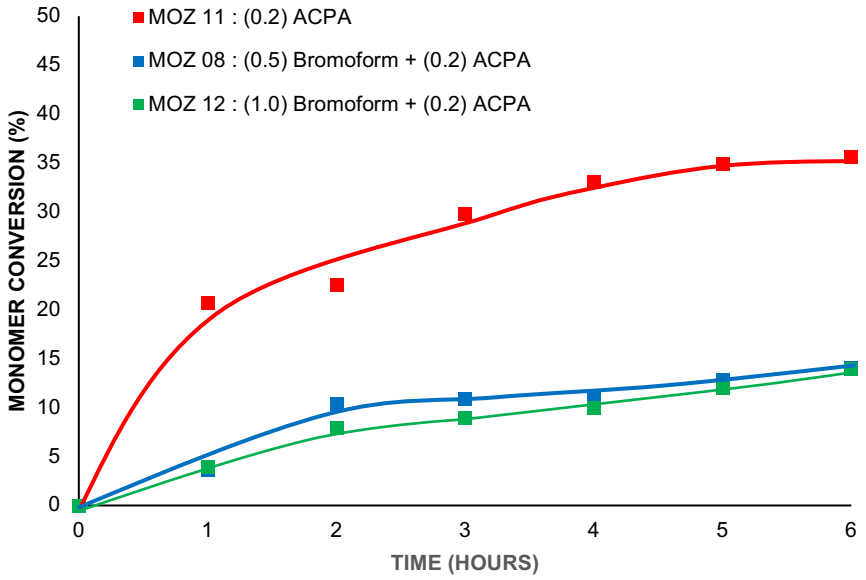


Figure 3.13. Monomer conversion *versus* time for the radical polymerisation of styrene using 0.2 molar equivalents ACPA with 0.5 and 1.0 molar equivalents bromoform in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

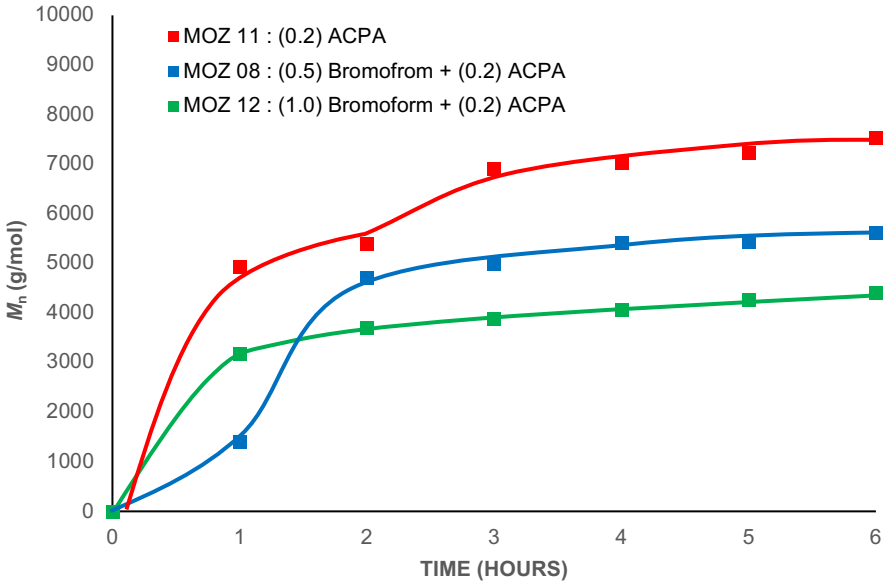


Figure 3.14. Polymer molar mass (M_n) *versus* time for the radical polymerisation of styrene using 0.2 molar equivalents ACPA with 0.5 and 1.0 molar equivalents bromoform in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

Figure 3.15 presents the molar mass and dispersity *versus* monomer conversion. The curves suggest a radical polymerisation, where 'high' molar mass polymers are obtained early in the reaction. Due to the reactions not reaching high conversions it is difficult to identify the role of bromoform under these conditions as the reaction using no bromoform had a similar molar mass. Figure 3.15 shows the dispersity remains slightly higher for the polymers produced using bromoform, compared to the reaction using ACPA only.

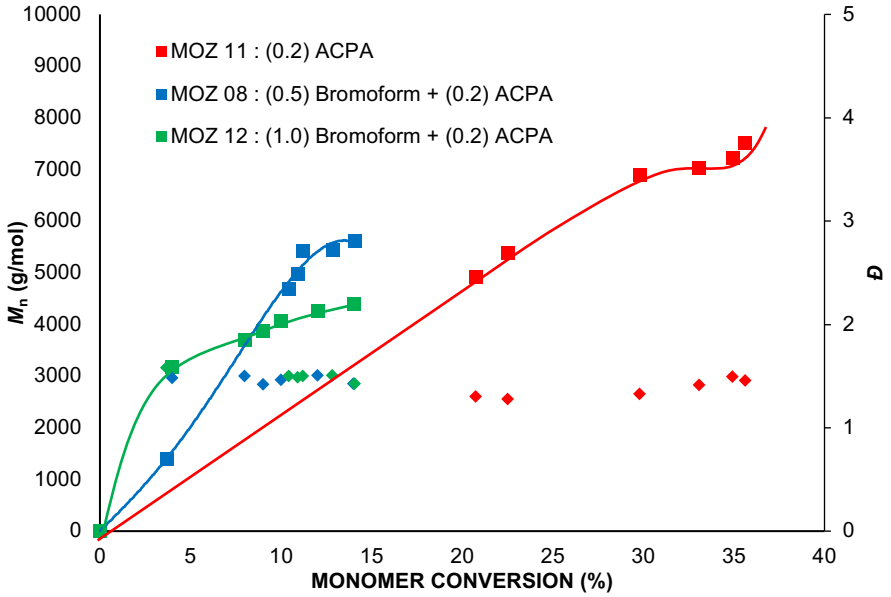


Figure 3.15. Molar mass (M_n, denoted by ■) and Dispersity ($Đ$, denoted by ◆ *versus* monomer conversion for the radical polymerisation of styrene using 0.2 molar equivalents ACPA with 0.5 and 1.0 molar equivalents bromoform in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

The semi-logarithmic plots, showing the first order dependence on monomer concentration, for each experiment are given in Figure 3.16. All experiments showed a two-stage linear progression. When comparing all three reactions, the largest apparent rate constant was observed for the polymerisation using ACPA. The first regime had an apparent rate constant equal to 0.233 h^{-1}, followed by a second slower regime. The reactions using 0.5 and 1,0 molar equivalents bromoform had an apparent rate constant equal to 0.052, and 0.042 h^{-1}, respectively. This is a significantly smaller apparent rate constant compared to the conventional radical polymerisation, this may suggest the addition of bromoform to this reaction results in fewer radicals being released into the system. The results from these experiments are not conclusive due to high conversions not being achieved. Therefore, it is not possible to ascertain any deviations occurs at high conversion. Also, if repeats were conducted on these experiments, the reaction may have shown a linear or multi progression instead of what has been identified.

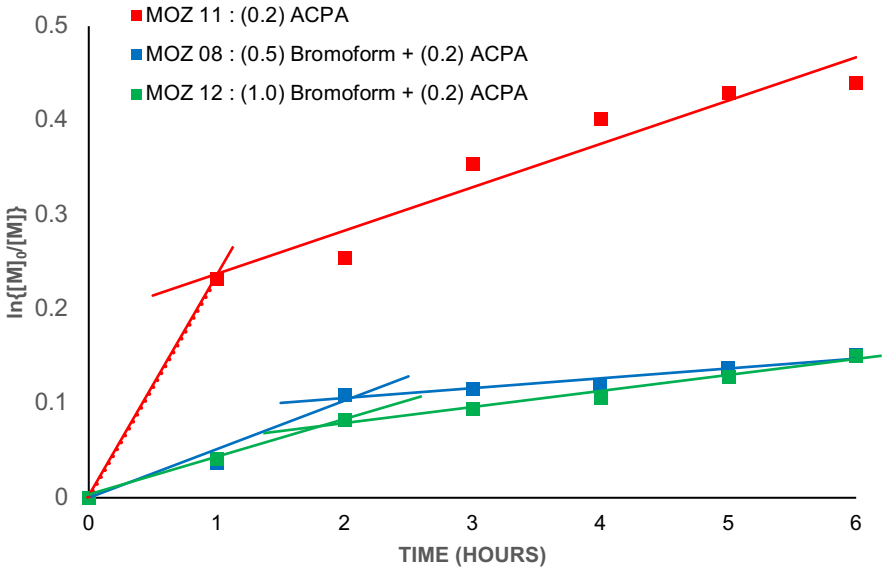


Figure 3.16. Semi-logarithmic plots for the radical polymerisation of styrene using 0.2 molar equivalents ACPA with 0.5 and 1.0 molar equivalents bromoform in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

3.3.1. Characterisation of PS prepared using bromoform under UV conditions

FTIR spectroscopy was performed on the precipitated polymers to identify the functional groups present in the final polymer. The resulting spectrum has been attached as Figure 3.17. The bands at 1453 and 1600 cm^{-1} are assigned to the stretching vibration of the benzene ring, the band at 700 cm^{-1} corresponds to the absorption of monosubstituted benzene. When comparing all three spectra no clear difference is observed and no information is visible on the end groups.

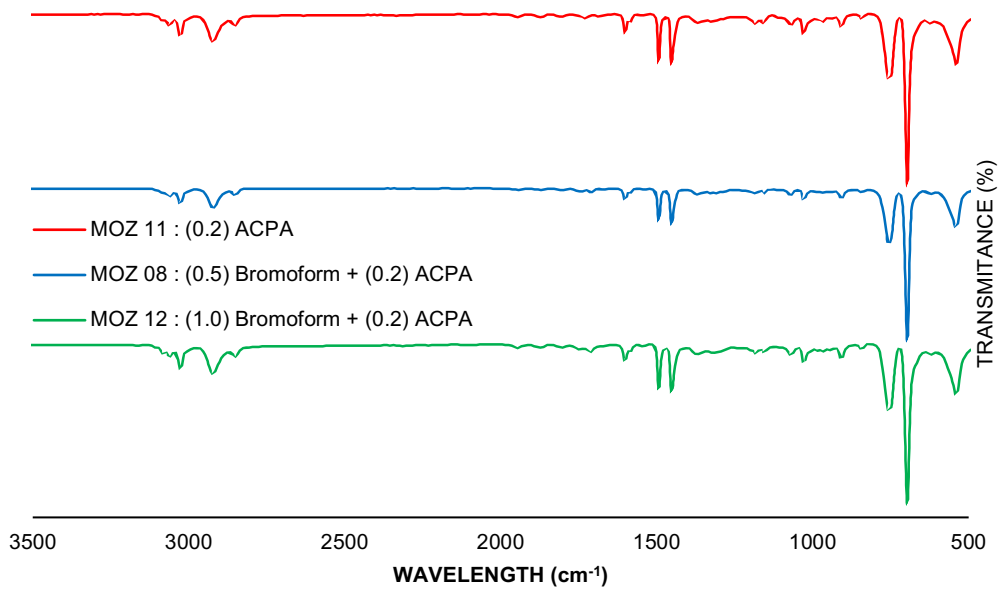


Figure 3.17. FTIR spectrum for the precipitated polymer produced from the radical polymerisation of styrene, using 0.2 molar equivalents ACPA and variable concentration of (0, 0.5, 1 molar equivalents) bromoform in 10 mL THF under UV light (λ = 100-400 nm) for 6 hours.

Figure 3.18 shows the DSC thermogram, for the resulting polymers produced. The thermogram shows the presence of one T_g, centred between 85-100 °C for all polymers. Polymers produced using bromoform had a higher T_g compared to the polymer produced using the conventional radical polymerisation. The addition of bromoform may result in polymers being produced with less branching. This is the opposite to the results obtained from the bromoform-mediated polymerisation under thermal conditions in Section 3.3.1. The main difference between both these experiments was the production of low molar mass polymers and low conversion being achieved under UV light. Literature has suggested the length of the polymer chain and branching can have a significant effect on the observed glass transition temperature.[108]

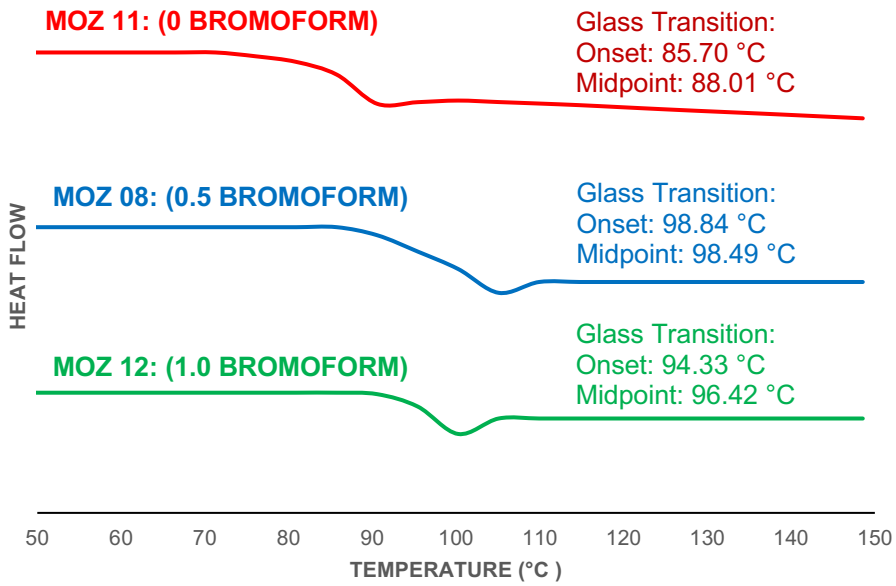


Figure 3.18. DSC thermogram for the polymers produced from the radical polymerisation of styrene, using 0.2 molar equivalents ACPA and variable concentration of (0, 0.5, 1 molar equivalents) bromoform in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

Figure 3.19 shows the ^{1}H NMR spectrum for the precipitated polymers from the conventional radical polymerisation and the bromoform-mediated polymerisation. The spectrum for all polymers consisted of 4 broad polymer resonance signals. This included two signals in the region of 7.56 ppm and 6.25 ppm which are characteristic of benzyl protons and signals around 2.23 ppm represent the methylene protons for PS. The spectrum for the polymer produced using 0.5 molar equivalents bromoform contained a series of signals between 3-4 ppm. These signals were assumed to arise from impurities present in the final polymer. The signal centred around 3.6 ppm is characteristic for residual THF in the polymer, and the peak at 3.3 ppm suggests the presence of methanol.

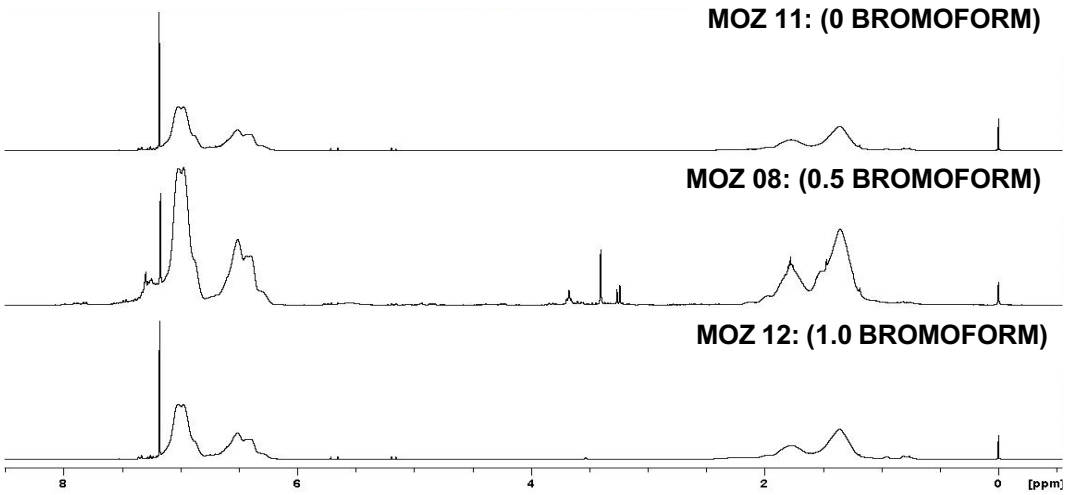


Figure 3.19. ^{1}H NMR spectrum (300 MHz) for the precipitated polymer produced from the radical polymerisation of styrene, using 0.2 molar equivalents ACPA and variable concentration of (0, 0.5, 1 molar equivalents) bromoform in 10 mL THF under UV light (λ = 100-400 nm) for 6 hours.

3.4. CONCLUSIONS

Section 3 focused on the bromoform-mediated polymerisation of styrene under thermal and UV conditions. The results from this chapter showed that bromoform may play an important role in the radical polymerisation of styrene. For the preparation of PS under thermal conditions, the addition of bromoform resulted in the production of low molar mass polymers which were closer to the target molar mass, when compared to the conventional radical polymerisation. Results from Section 3.2 showed the bromoform-mediated polymerisation proceeds via a radical mechanism, where 'high' molar mass polymers are produced early in the reaction.

Results from the UV experiments suggest, under the current experimental conditions, that bromoform does not behave as a photo-initiator, which Miller[2] had suggested. The main difference between Miller's research and this project is the solvent used. Miller conducted the polymerisation of acrylonitrile in an equal volume bromoform, whereas in this project THF was used as the reaction solvent. The results from the experiments showed it was difficult to obtain high conversion and therefore the behaviour of bromoform under UV light is still unknown. High conversions were not achievable due to the slow propagation rate coefficient of styrene (k_p (30 °C) = 106 dm^3 mol^{-1} s^{-1}).[109] To further investigate the behaviour of bromoform a wider range of experiments should be designed using different quantities of bromoform and initiator with a monomer which has a faster propagating rate.

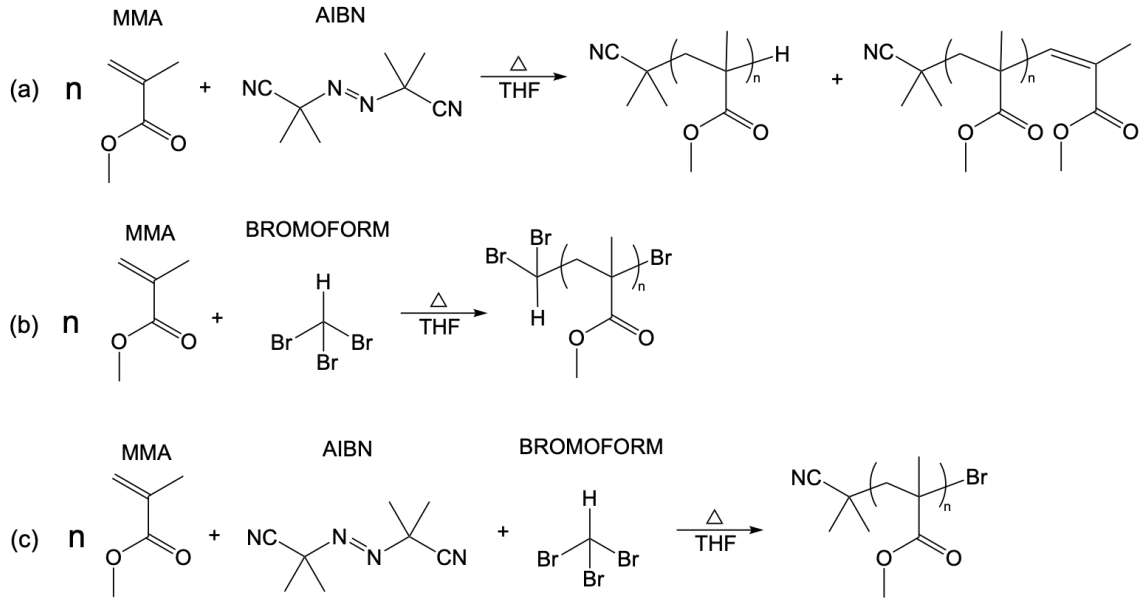
Accordingly, Chapter 4 focuses on the polymerisation of MMA using bromoform under both thermal and UV conditions. The propagation rate coefficient for MMA monomer at 30 °C is equal to 390 dm^3 mol^{-1} s^{-1},[109] which is significantly larger than the propagation rate coefficient of styrene.

CHAPTER 4

PREPARATION OF POLY(METHYL METHACRYLATE) UNDER THERMAL AND ULTRAVIOLET CONDITIONS

4.1. THE EFFECT BROMOFORM HAS ON THE RADICAL POLYMERISATION OF MMA UNDER THERMAL CONDITIONS

The results reported in Chapter 3 suggest that the addition of bromoform has a marked effect on the radical polymerisation of styrene. The experiments under UV conditions were less conclusive due to low conversions being reached. Chapter 4 focuses on the polymerisation of MMA under thermal and UV conditions. The experiments from Section 3.3 were repeated using MMA and using a larger range of experiments. The experiments conducted included the following: a conventional radical polymerisation using AIBN, a reaction where bromoform is used as a thermal initiator and a series of polymerisation reactions where bromoform is added to the conventional radical polymerisation. For the last set of experiment, a range between 0.1 to 2 molar equivalents of bromoform was added as a possible CTA. The reaction scheme for these experiments has been outlined in Scheme 4.1. The structure of the end groups have been outlined from the following assumptions: (a) MMA does not undergo self-initiated polymerisation, the reaction proceeds via termination by disproportionation (for convenience purpose), (b) bromoform behaves as a thermal initiator by the thermal decomposition of bromoform, and both radicals can behave as the initiating radical and (c) bromoform behaves as a CTA which produces polymers with bromine end groups.



Scheme 4.1. Synthesis of PMMA using: AIBN as a thermal initiator (a), bromoform as a thermal initiator (b) and bromoform as a CTA with AIBN (d). The reactions were conducted in 10 mL THF at 70 °C for 24 hours. For simplicity only major products are shown.

The molar mass and monomer conversion data for these reactions are shown in Table 4.1. Overall, monomer conversion above 96 % was achieved for all reactions where bromoform was added to the conventional radical polymerisation. Literature and the experimental results show MMA does not undergo self-initiated thermal polymerisation at 70 °C.[110] The addition of bromoform to the conventional radical polymerisation system, shows the production of low molar mass polymers closer to the target M_n. This observation is similar to the results reported in Section 3.2, for the thermal polymerisation of styrene. From the new experiments, a clear trend can be noticed between increasing the concentration of bromoform and the observed molar mass. The results shows a significant difference between the theoretical M_n and the actual M_n. This could suggest bromoform can behave as a transfer agent and offers some control over the molar mass compared to the conventional radical polymerisation. The molar mass data shows the polymers produced using bromoform have slightly lower dispersity compared to the polymers produced using conventional radical polymerisation, but a clear trend between increasing the concentration of bromoform is not visible.

Table 4.1. Molar mass data for the polymerisation of 5 g (50 mmol) MMA using 0.2 molar equivalents AIBN with 0.1-2.0 molar equivalents bromoform in 10 mL THF. The reactions were conducted at 70 °C for 24 hours.

Code	Molar equivalents of bromoform added	Molar equivalents of AIBN added	Theoretical M_n (g/mol) (a)	Monomer conversion (%) (b)	Observed M_n (g/mol) ©	$Đ$ ©	k_{app} (h^{-1}) (d)
MOZ 15	0	0	-	0	-	-	-
MOZ 17	0	0.2	-	99	58,000	1.66	0.310
MOZ 29	0.1	0.2	40,000	99	33,000	1.55	0.310
MOZ 30	0.2	0.2	20,000	99	31,000	1.57	0.300
MOZ 19	0.5	0.2	8,000	99	29,000	1.61	0.230
MOZ 18	1.0	0.2	4,000	99	24,000	1.56	0.230
MOZ 31	2.0	0.2	2,000	96	20,000	1.60	0.260

(a) Molar equivalents of MMA = 40, theoretical M_n based on the assumption bromoform behaves as a CTA similar to RAFT polymerisation.

(b) Monomer conversion was determined by ^{1}H NMR spectroscopy.

(c) M_n and $Đ$ determined by GPC [poly(methyl methacrylate) standards].

(d) The apparent rate constant (measured by ^{1}H NMR spectroscopy).

(e) Experiments were carried out once, due to limited time constraints.

The kinetics for the reactions were followed by GPC and ^{1}H NMR spectroscopy, from the samples taken every hour for the first 6 hours and one after 24-hours. The reactions were stopped after 24 hours, due to solvent evaporation and simultaneous polymerisation which increases the reaction medium viscosity and therefore the stirring to stop. The plots of monomer conversion *versus* time are shown in Figure 4.1 and molar mass *versus* time in Figure 4.2. Figure 4.1 shows the addition of bromoform results in high monomer conversion (> 90 %) being achieved slightly slower compared to the experiments using only AIBN. This is the opposite effect Section 3.2, for the polymerisation of styrene using bromoform. Figure 4.2 shows for all concentration of bromoform added the observed molar mass is much lower compared to the conventional radical polymerisation. This is a similar pattern to the bromoform-mediated polymerisation of styrene.

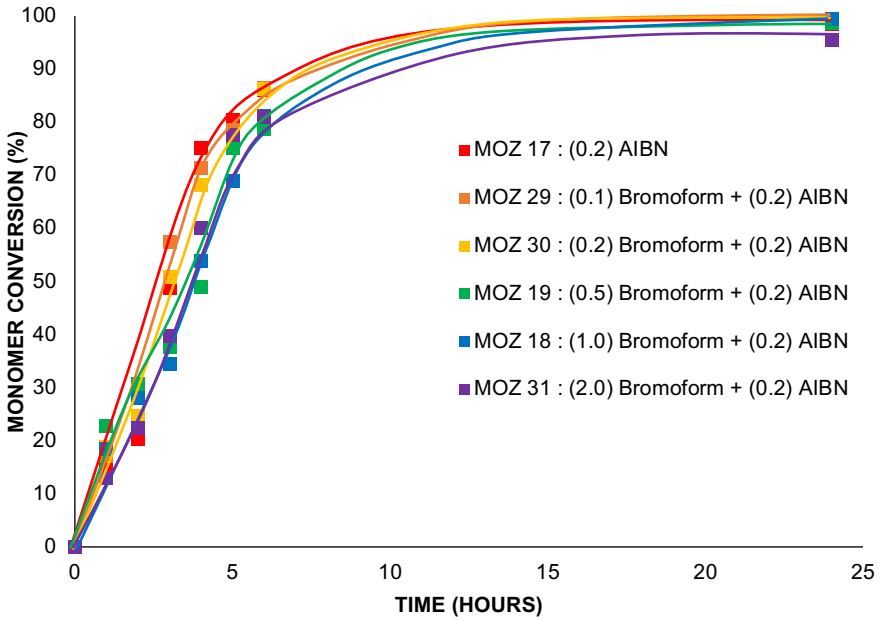


Figure 4.1. Monomer conversion *versus* time for the radical polymerisation of MMA using 0.2 molar equivalents AIBN with 0.1-2.0 molar equivalents bromoform in 10 mL THF. The reactions were conducted at 70 °C for 24 hours.

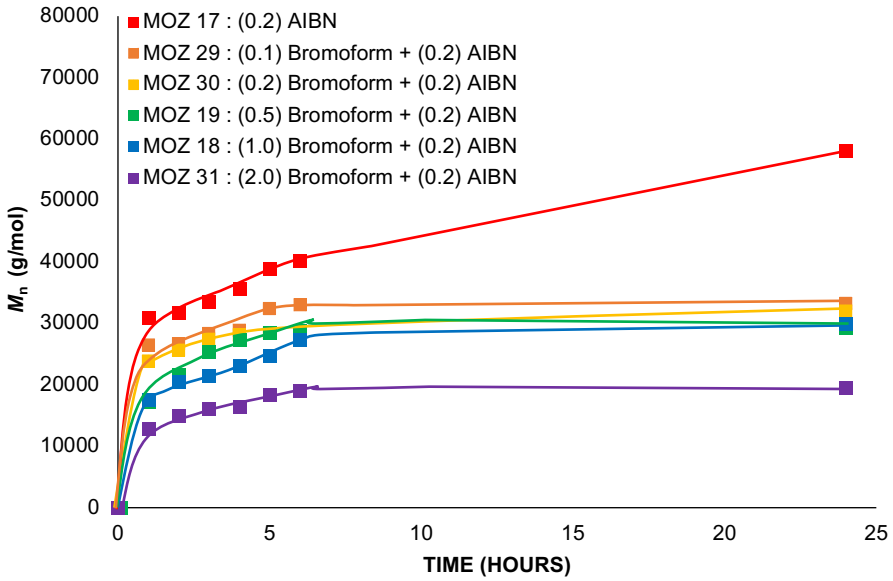


Figure 4.2. Molar mass (M_n) *versus* time for the radical polymerisation of MMA using 0.2 molar equivalents AIBN with 0.1-2.0 molar equivalents bromoform in 10 mL THF. The reactions were conducted at 70 °C for 24 hours.

Figure 4.3 presents the molar mass *versus* monomer conversion. The data shown in Figure 4.3 shows a clear trend between increasing the concentration of bromoform and the observed molar mass. For conventional radical polymerisation, a rapid increase in molar mass is observed around 80 % conversion. This may suggest a termination reaction which leads to the production of high molar mass polymers.

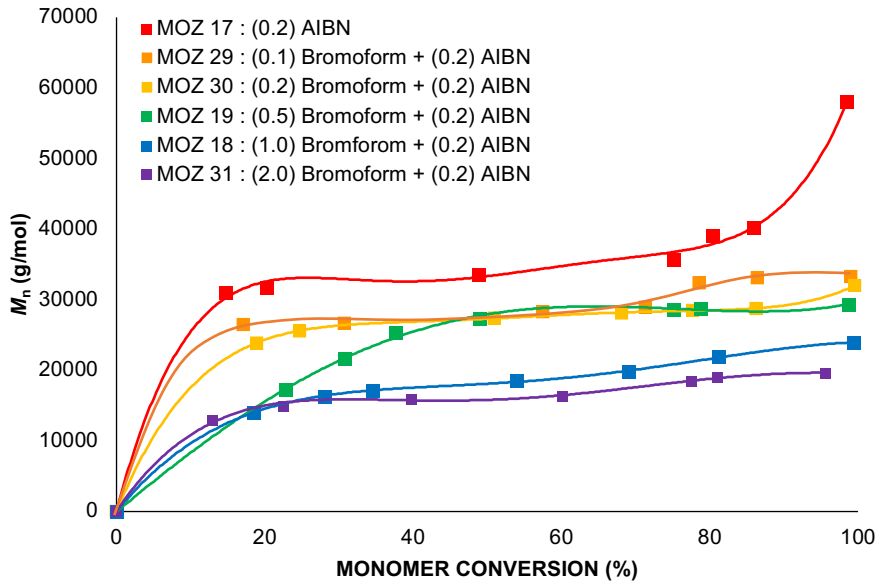


Figure 4.3. Molar mass (M_n) *versus* monomer conversion for the radical polymerisation of MMA using 0.2 molar equivalents AIBN with 0.1-2.0 molar equivalents bromoform in 10 mL THF. The reactions were conducted at 70 °C for 24 hours.

The semi-logarithmic plots, showing the first order dependence on monomer concentration, are shown in Figure 4.4. All experiments showed a two-stage progression. The largest apparent rate constant was observed for conventional radical polymerisation. The smallest apparent rate constant observed was for the reaction using 0.5 and 1.0 molar equivalents bromoform, both with an apparent rate constant of 0.23 h^{-1}. This may suggest the addition of bromoform to the reaction, results in fewer radicals being released into the system compared to the conventional radical polymerisation. This is opposite to what was observed in Section 3.2. The trend between increasing the concentration of bromoform and the apparent rate constant is not clear. For example, the reaction using the largest quantity of bromoform had an apparent rate constant of 0.26 h^{-1}, which is larger than the reaction using 0.5 and 1.0 molar equivalents. To ensure the observations are accurate repeats of each experiment should be conducted to identify possible outliers. Figure 4.3 clearly shows a second slower polymerisation regime, with a smaller apparent rate constant compared to the first stage. This could suggest a termination step/reaction or a slower polymerisation rate due to poor mixing as a result of an increase to the viscosity of the reaction medium.

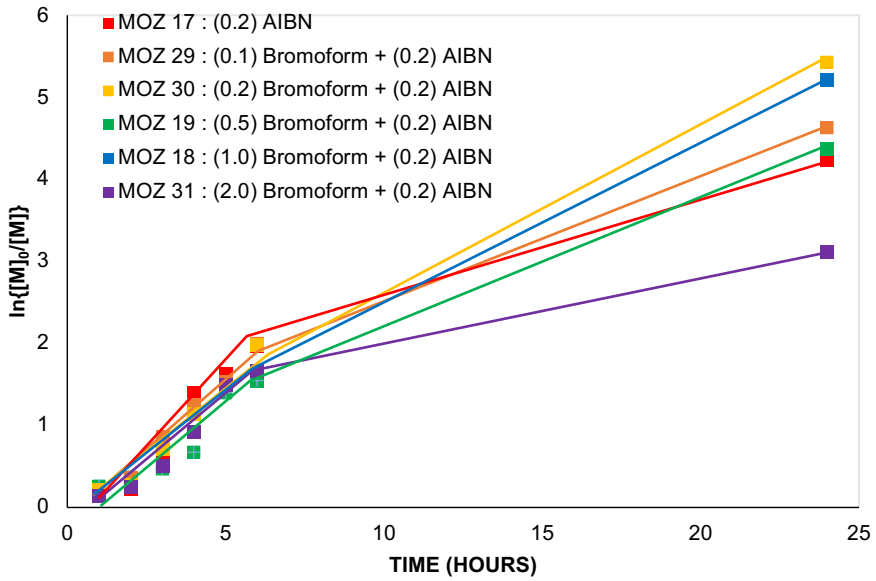


Figure 4.4. Semi-logarithmic plots for the radical polymerisation of MMA using 0.2 molar equivalents AIBN with 0.1-2.0 molar equivalents bromoform in 10 mL THF at 70 °C for 24 hours.

4.1.1. Characterisation of PMMA prepared using bromoform under thermal conditions.

This section gives detail on the results obtained for the characterisation of the polymers produced using conventional radical polymerisation and 0.5 and 1.0 molar equivalents bromoform. The characterisation techniques used include the following: FTIR, DSC and NMR.

FTIR spectroscopy was used to identify the main functional groups present in the final polymers. The spectrum for the polymers produced using conventional radical polymerisation and the polymers produced using 0.5 and 1.0 molar equivalents bromoform is shown in Figure 4.5. The spectrum contained a strong C=O carbonyl stretch at 1730 cm^{-1}, O-CH_3 and C-O bending at 1250 and 1150 cm^{-1}. These bands are all characteristic for the ester group present in PMMA. The C-H vibrations around 1400 cm^{-1} and 2995 cm^{-1}, which are characteristic for the methyl and methylene stretch. When comparing all three spectra show no clear difference is observed and no information is visible on the end groups.

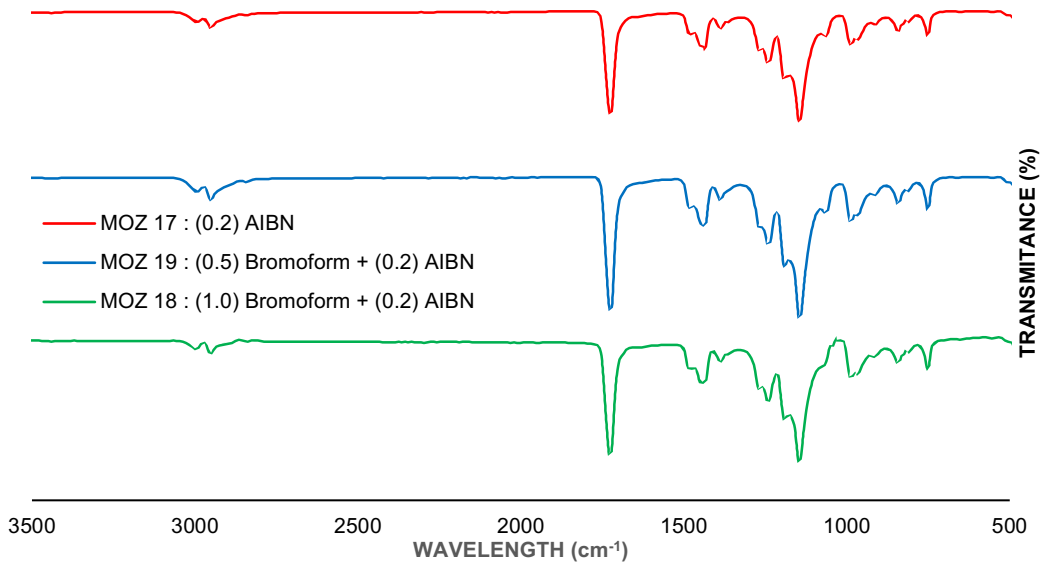


Figure 4.5. FTIR spectrum for he precipitated polymers produced from the radical polymerisation of MMA, using 0.2 molar equivalents AIBN and variable concentration of (0, 0.5, 1 molar equivalents) bromoform in 10 mL THF. The reactions were conducted at 70 °C for 24 hours.

DSC was used to determine the T_g for the polymer produced using conventional radical polymerisation and using 0.5 and 1.0 molar equivalents bromoform. The resulting DSC thermograms are shown in Figure 4.6. The thermogram for the polymers produced show one T_g, centred between 130-135 °C. Polymers produced using bromoform showed a slightly higher T_g compared to the polymer produced under conventional radical polymerisation. However, this is is not clear as each polymer have different M_n and lengths.

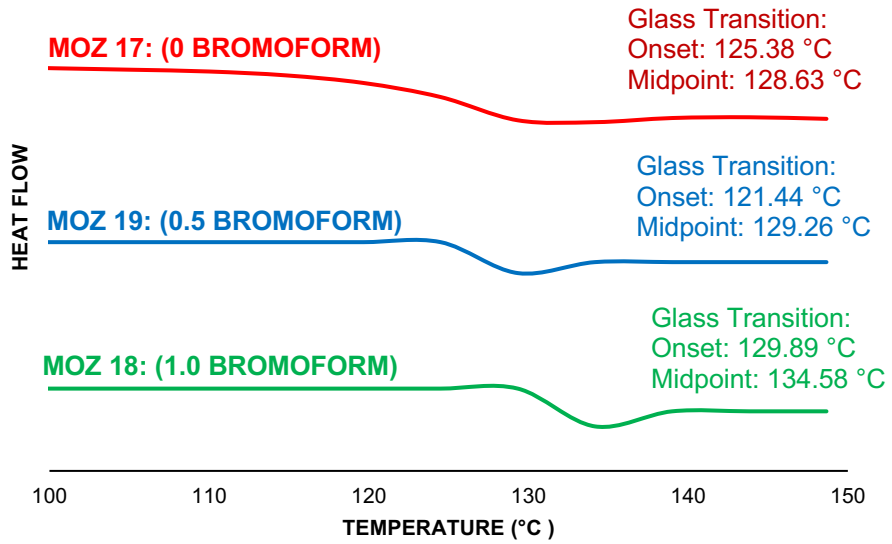


Figure 4.6._DSC thermogram for the final heating cycle for the precipitated polymers produced from the radical polymerisation of MMA, using 0.2 molar equivalents AIBN and variable concentration of (0, 0.5, 1 molar equivalents) bromoform in 10 mL at 70 °C.

Figure 4.7 outlines the ^{1}H NMR spectrum for the precipitated polymers (in $CDCl_3$) using 0, 0.5 and 1 molar equivalents bromoform in the radical polymerisation of MMA (*i.e.* with AIBN). The spectrum for the polymers contained 4 broad polymer resonance signals. The signal at 3.55 ppm is attributed to the methyl ester group of PMMA. The signal in the region ranging from 1.65 to 1.95 ppm and 0.65 to 1.02 ppm are attributed to the methylene and methyl group of atactic PMMA, respectively. All three spectrum look essentially the same, and no information on end groups is visible.

Figure 4.7. ^{1}H NMR (300 MHz) spectrum for the precipitated polymers produced from the radical polymerisation of MMA using 0.2 molar equivalents AIBN and variable concentration of (0, 0.5, 1 molar equivalents) bromoform in 10 mL at 70 °C.

4.2. THE EFFECT AIBN HAS ON THE BROMOFORM-MEDIATED POLYMERISATION OF MMA UNDER THERMAL CONDITIONS

The results reported in Section 4.1 suggest bromoform offers some control over molar mass. In this section 1.0 molar equivalents bromoform was used for the polymerisation of MMA with various quantity of AIBN. For the first experiment, bromoform was used alone to identify if it can act as a thermal initiator at 70 °C. A series of experiments, were designed using bromoform and various quantities of AIBN. For these experiments a range between 0.1 to 1 molar equivalents of AIBN were added as a thermal initiator. The molar mass and monomer conversion data for these experiments are listed in Table 4.2. Overall, high monomer conversion (> 90 %) was achieved for all reactions. The results initially shows that bromoform can behave as a thermal initiator at 70 °C for the polymerisation of MMA in THF. Section 3.2 showed this was not possible for the polymerisation of styrene under the same conditions. This could suggest that bromoform can undergo thermolysis and react with a monomer unit to form a macro radical. Due to the faster propagating rate of MMA compared to styrene, polymers can be produced using this method, this is explored further in Section 4.3. High conversion and polymers which had molar mass close to the target M_n was obtained when using bromoform only. The results show increasing the concentration of AIBN added, results in low molar mass polymers being formed. Literature reports have stated, increasing the concentration of the initiator results in the production of more reactive initiating radicals, therefore more propagating chains are present in the system, and as a result, low molar mass polymers are obtained.[111]

Table 4.2. Molar mass data for the polymerisation of 5 g (50 mmol) MMA using 1 molar equivalents bromoform with 0-1.0 molar equivalents AIBN. The reactions were conducted in 10 mL THF at 70 °C for 24 hours.

Code	Molar equivalents of AIBN added	Monomer conversion (%) [(a)]	Observed M_n (g/mol) [(b)]	$Đ$ [(b)]	k_{app} (h^{-1}) [©]
MOZ 16	0	94	9,700	1.55	0.300
MOZ 32	0.1	99	38,000	1.96	0.300
MOZ 18	0.2	99	24,000	1.56	0.230
MOZ 33	0.5	98	16,000	1.59	0.340
MOZ 34	1.0	99	12,000	1.65	0.570

(a) Monomer conversion determined by ^{1}H NMR spectroscopy

(b) M_n and $Đ$ determined by GPC [poly(methyl methacrylate) standards]

(c) The apparent rate constant (measured by ^{1}H NMR spectroscopy)

(d) Experiments were conducted once, due to limited time constraints.

The reactions were stopped after 24 hours, due to solvent evaporation and simultaneous polymerisation which increased the viscosity of the reaction medium and therefore the stirring to stop. The plots of monomer conversion *versus* time are shown in Figure 4.8 and molar mass *versus* time in Figure 4.9. Figure 4.8 shows increasing the quantity of AIBN added, results in high monomer conversions being reached earlier in the reaction. For example, when 1.0 molar equivalents AIBN is added 90 % monomer conversion is achieved within 5 hours, compared to when 0.1 molar equivalents were added the conversion is 80 %. When 0.1 and 0.2 molar equivalents AIBN is used, the lower conversion is reached after 6 hours compared to when no AIBN. Both reactions reached 98 % conversions within 24 hours. The difference is not conclusive as there may be some anomalies present, therefore the experiments should be repeated to identify a clear trend. Figure 4.9 shows the largest molar mass observed was for when 0.1 molar equivalents AIBN was added, and the lowest for when bromoform is used as a thermal initiator.

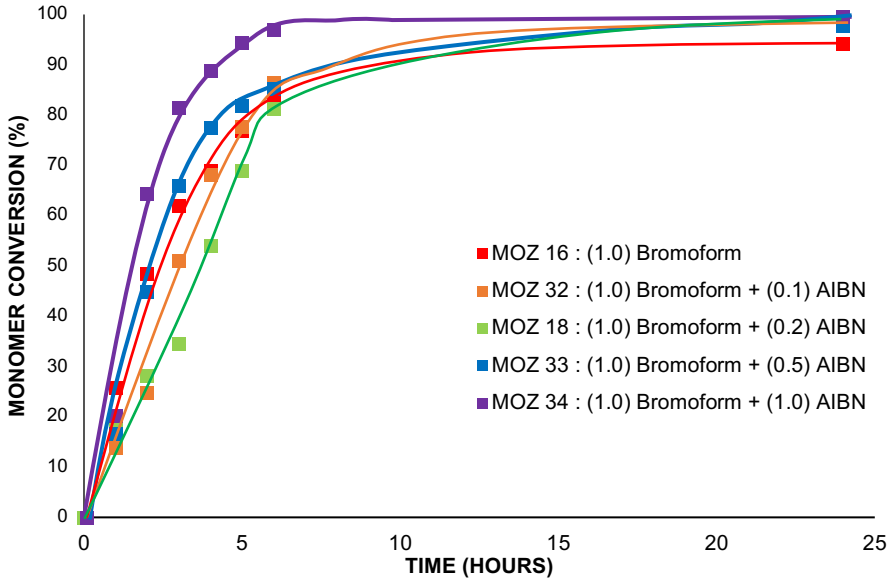


Figure 4.8. Monomer conversion *versus* time for the radical polymerisation of MMA using 1.0 molar equivalents bromoform and 0-1.0 molar equivalents AIBN in 10 mL THF. The reactions were conducted at 70 °C for 24 hours.

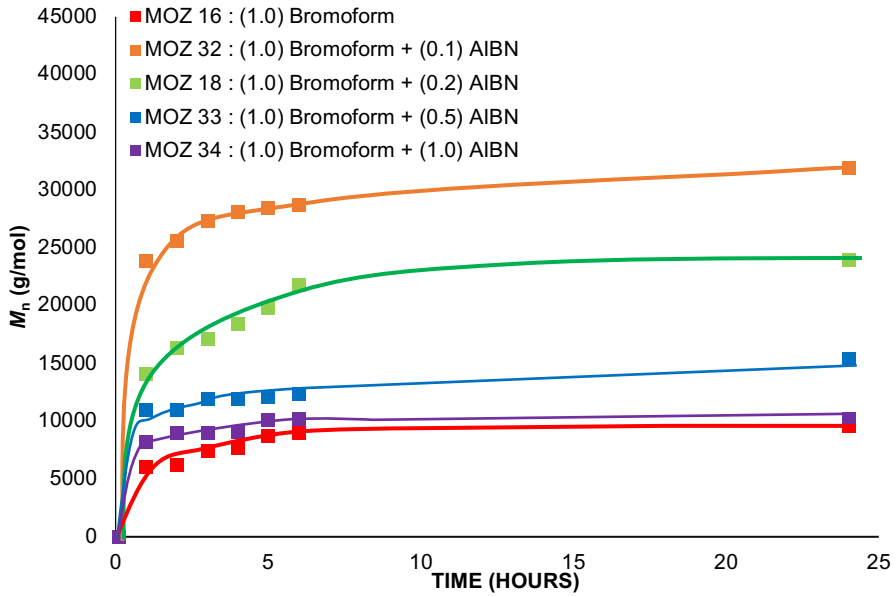


Figure 4.9. Molar mass (M_n) *versus* time for the radical polymerisation of MMA using 1.0 molar equivalents bromoform and 0-1.0 molar equivalents AIBN in 10 mL THF. The reaction was conducted at 70 °C for 24 hours.

Figure 4.10 shows the molar mass *versus* monomer conversion for these experiments. The graph shows a clear trend between increasing the quantity of AIBN and the observed molar mass. The results show using 1 molar equivalents of bromoform as an initiator produces low molar mass polymers which are closer to the target molar mass. For experiments using less than 0.5 molar equivalents AIBN we notice a significant increase in molar mass above 80 % conversion, this may suggest a termination reaction.

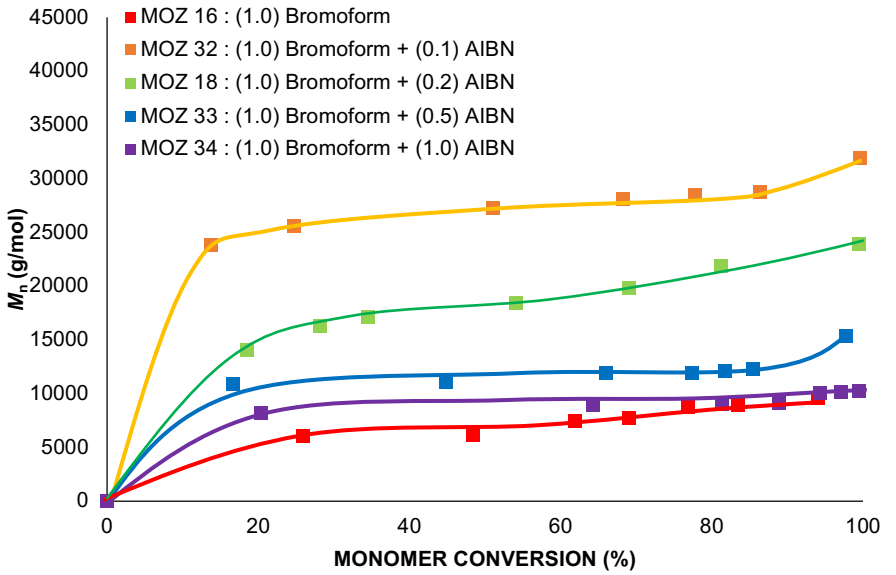


Figure 4.10. Molar mass (M_n) *versus* monomer conversion for the radical polymerisation of MMA using 1.0 molar equivalents bromoform and 0-1.0 molar equivalents AIBN in 10 mL THF. The reactions were conducted at 70 °C for 24 hours.

The semi-logarithmic plots, showing the first order dependence on monomer concentration, are given in Figure 4.11. The experiments show two-stage progression for all reactions, indicating a change in radical concentration across time. The largest apparent rate constant was observed for the reaction using 1 molar equivalents AIBN, as expected. The smallest apparent rate constant was observed for the experiment using 0.2 molar equivalents AIBN which had an apparent rate constant of 0.230 h^{-1}. The results show increasing the quantity of AIBN, leads to a larger apparent rate constant being observed. Increasing the quantity of AIBN added results in more radicals being released into a system, and as a result a larger rate constant should be observed. The results from using 0.2 molar equivalents AIBN does not fit this trend which may suggest the results from this experiment contains a few anomalies, therefore the experiments should be repeated to ensure all results are accurate.

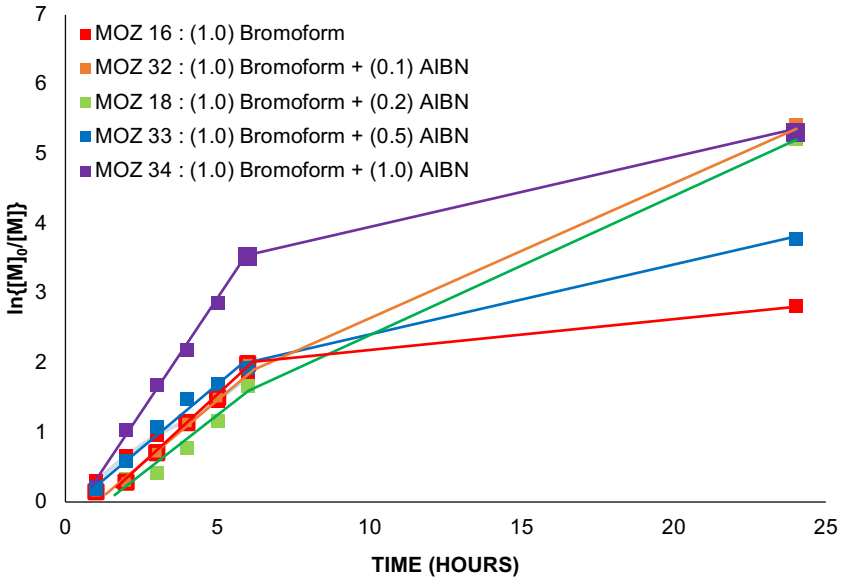


Figure 4.11. Semi-logarithmic plots for the radical polymerisation of MMA using 1.0 molar equivalents bromoform and 0-1.0 molar equivalents AIBN in 10 mL THF. The reactions were conducted at 70 °C for 24 hours.

4.3. THE POLYMERISATION OF MMA USING BROMOFORM AS A THERMAL INITIATOR

The results from Section 4.2 suggested bromoform can behave as a thermal initiator for the polymerisation of MMA at 70 °C in THF. Experiments were designed using 0.1 to 1 molar equivalents of bromoform only. The molar mass and monomer conversion data for these reactions are shown in Table 4.3. Overall, high monomer conversion (> 85 %) was achieved for all reactions. The results show increasing the quantity of bromoform added results in low molar mass polymers being produced, which are closer to the target molar mass. Table 4.2 shows bromoform is directly involved in the polymerisation, as the negative control shows MMA doesn't undergo self-initiated thermal polymerisation at 70 °C in THF.

Table 4.3. Molar mass data for the polymerisation of 5 g (50 mmol) MMA using 0.1–1.0 molar equivalents bromoform as a thermal imitator in 10 mL THF. The reactions were conducted at 70 °C for 24 hours.

Code	Molar equivalents of bromoform added	Monomer conversion (%) [(a)]	Actual DP [(b)]	Observed M_n (g/mol) [(b)]	$Đ$ [(b)]	k_{app} (h^{-1}) [©]
MOZ 15	0	0	-	-	-	-
MOZ 41	0.1	88	330	33,000	1.53	0.180
MOZ 42	0.2	88	210	21,000	1.49	0.230
MOZ 43	0.3	88	180	18,000	1.53	0.250
MOZ 44	0.4	87	160	16,000	1.51	0.220
MOZ 45	0.5	87	100	10,000	2.08	0.250
MOZ 16	1.0	94	97	9,700	1.55	0.300

(a) Monomer conversion determined by ^{1}H NMR spectroscopy

(b) M_n and $Đ$ determined by GPC [poly(methyl methacrylate) standards]

(c) The apparent rate constant (measured by ^{1}H NMR spectroscopy)

(d) Experiments were carried out once, due to limited time constraints.

The kinetics for the reactions were followed by GPC and ^{1}H NMR spectroscopy, with samples taken at various times for 24 hours. The reactions were stopped after 24 hours, due to solvent evaporation and simultaneously polymerisation which resulted in an increase in the reaction medium viscosity and therefore the stirring to stop. The plots of monomer conversion *versus* time are shown in Figure 4.12 and molar mass *versus* time in Figure 4.13. Figure 4.12 shows increasing the concentration of bromoform results in high monomer conversion being reached earlier in the reaction. For example, when 1.0 molar equivalents of bromoform is added, 80 % monomer conversion is achieved within 5 hours. When 0.1 molar equivalents was used, around 60 % conversion was achieved in the same time. The difference between each curve is marginal, therefore it's difficult to conclude the extent of increasing the concentration of bromoform by 0.1 molar equivalents has on the conversion. Figure 4.13 shows a clear trend between increasing the molar equivalents of bromoform added and the observed molar mass. The graph shows increasing the quantity of bromoform results in low molar mass polymers being produced. This could suggest increasing the concentration of bromoform results in more initiating radicals being produced, and as a result, more monomer units are being consumed and smaller chains are being produced. This could suggest bromoform can behave as an initiator and as a transfer agent or a capping agent based on the results from Section 4.1.

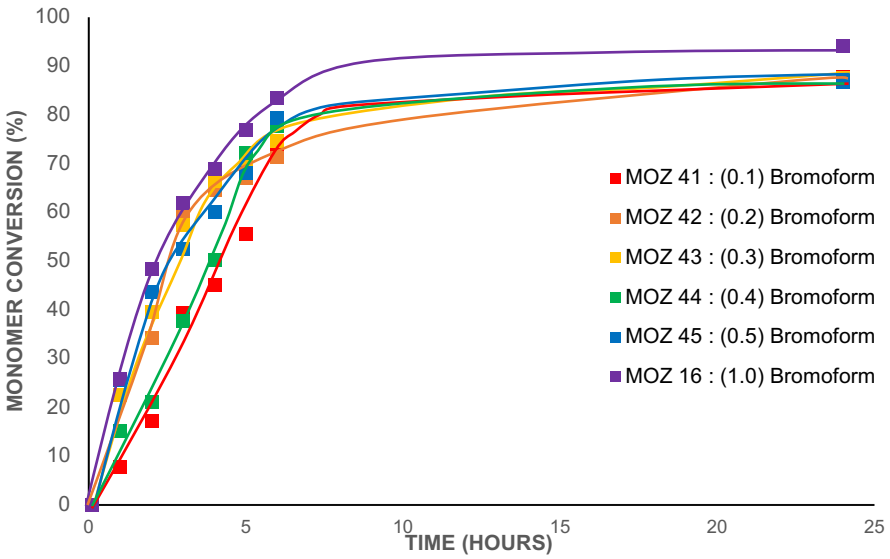


Figure 4.12. Monomer conversion *versus* time for the radical polymerisation of MMA using 0.1-1.0 molar equivalents bromoform as a thermal imitator in 10 mL THF. The reactions were conducted at 70 °C for 24 hours.

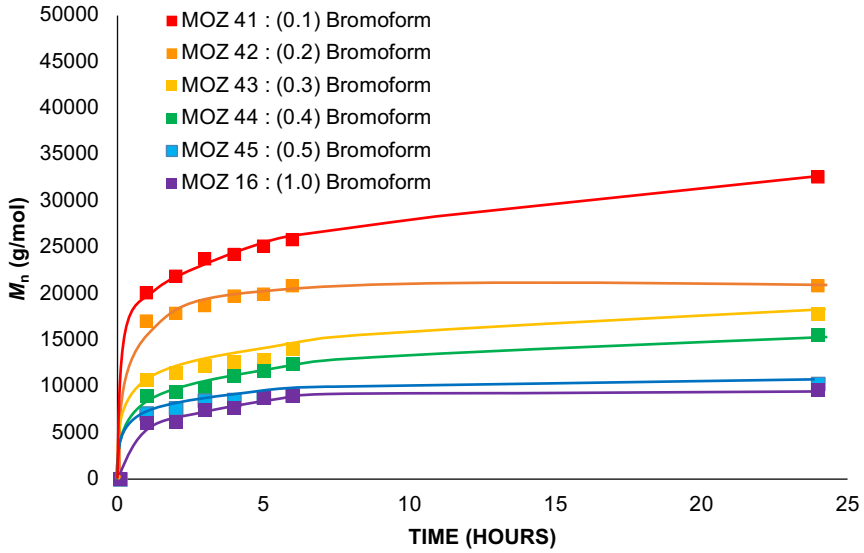


Figure 4.13. Molar mass (M_n) versus time for the radical polymerisation of MMA using 0.1-1.0 molar equivalents bromoform as a thermal imitator in 10 mL THF. The reactions were conducted at 70 °C for 24 hours.

Figure 4.14 shows the molar mass *versus* monomer conversion for these experiments. The graph suggests 'high' molar mass polymers are achieved early in the reaction. The graphs shows a significant increase in molar mass for the majority of the curves, when the conversion is above 80 %. This is well studied for PMMA and is characteristic for the termination reaction, which results in the formation of high molar mass polymers.[112]

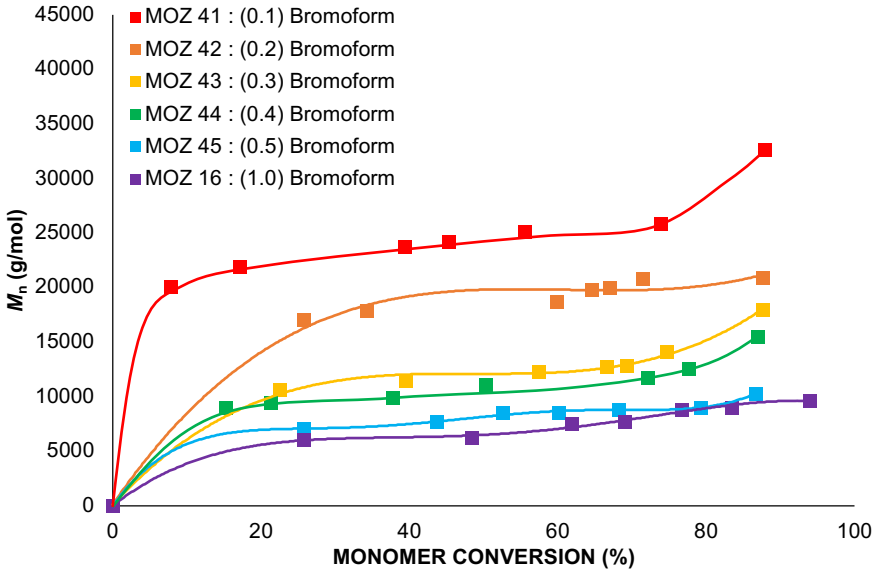


Figure 4.14. Molar mass (M_n) *versus* monomer conversion for the radical polymerisation of MMA using 0.1-1.0 molar equivalents bromoform as a thermal imitator in 10 mL THF. The reactions were conducted at 70 °C for 24 hours.

The semi-logarithmic plots, showing the first order dependence on monomer concentration are shown in Figure 4.15. The reactions show two-stage linear progression for all experiments, indicating a change in radical concentration across time. The largest apparent rate constant was observed for the reaction using 1.0 molar equivalents bromoform. The smallest observed was for the reaction using 0.1 molar equivalents bromoform. However, the graph contains data points which don't fit the trend lines; therefore, the results might not be accurate. To ensure the results are valid, the experiments should be repeated, and any outliers should be removed. For all reactions, a slower polymerisation regime is observed, which may suggest a termination step/reaction.

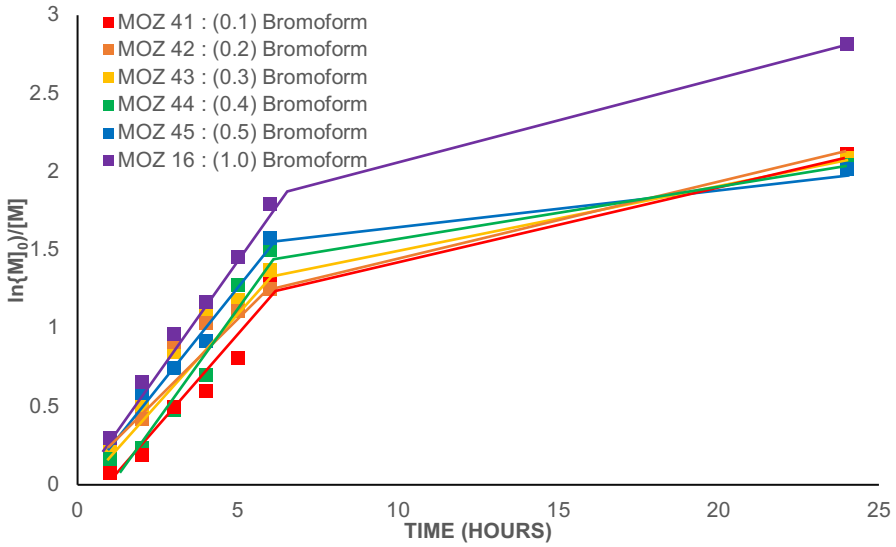


Figure 4.15. Semi-logarithmic plots for the radical polymerisation of MMA using 0.1-1.0 molar equivalents bromoform as a thermal imitator in 10 mL THF. The reactions were conducted at 70 °C for 24 hours.

4.3.1. The effect oxygen has on the polymerisation of MMA using bromoform as a thermal initiator

To understand the conditions required for bromoform to behave as a thermal initiator, the reaction was repeated without removing oxygen. Oxygen is a well-known radical scavenger and acts as an inhibitor in radical polymerisation.[113] For this reaction 1.0 molar equivalents bromoform was used to polymerise 5 g MMA in 10 mL THF at 70 °C. For this experiment, the reaction flask was sealed with a rubber septum to reduce solvent evaporation. Samples were taken every hour for the first 6 hours and one sample at 24 hours for kinetics studies. The results from this experiment were compared to the reaction conducted under nitrogen.

The plots of monomer conversion *versus* time for the reaction conducted in nitrogen and in air are shown in Figure 4.16 and Figure 4.17 shows the molar mass *versus* time for both reactions. Figure 4.16 and 4.17 show the reaction conducted in air has a 3-hour induction period where monomer conversion and molar mass remains low. Following this period, the reaction starts to proceed, after 24 hours conversion was less than 40 %. Figure 4.17 shows 'high' molar mass polymers are formed after the induction period. This suggests for the first 3 hours, oxygen is reacting with the initiating radicals, which normally start chain propagation. Following this period, we can assume the effect of oxygen being present in the system has been overwritten and the reaction starts to proceed. When the reaction is conducted in air high conversions are not achieved, when compared to the reaction conducted under nitrogen.

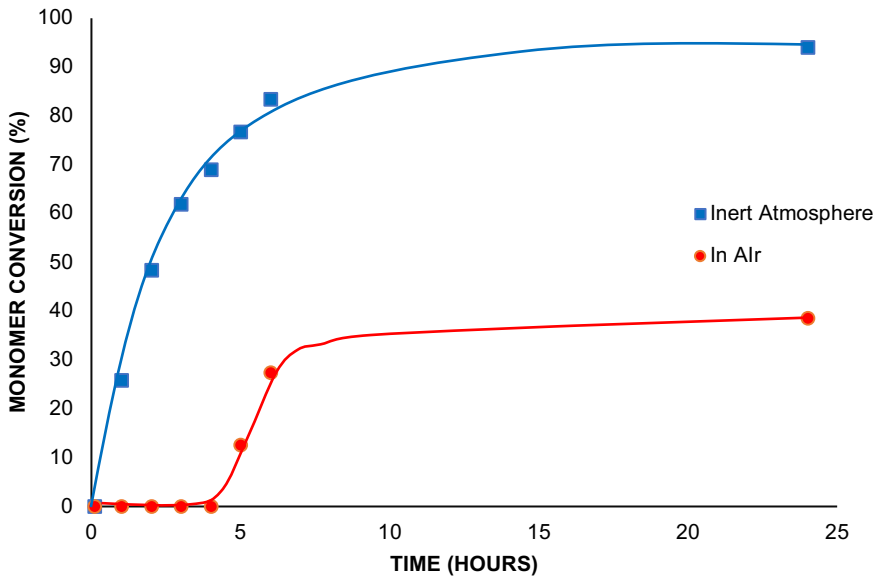


Figure 4.16. Monomer conversion *versus* time for the radical polymerisation of 5 g (50 mmol) MMA using 1.0 molar equivalents bromoform as a thermal imitator in 10 mL THF at 70 °C. The reactions were conducted under nitrogen and in air for 24 hours.

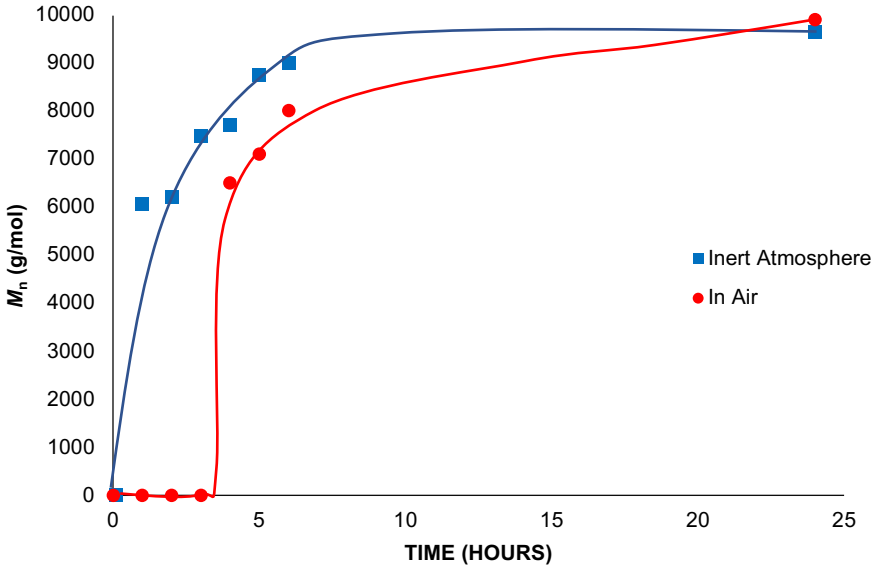


Figure 4.17. Molar mass (M_n) *versus* time for the radical polymerisation of 5 g (50 mmol) MMA using 1.0 molar equivalents bromoform as a thermal imitator in 10 mL THF at 70 °C. The reactions were conducted under nitrogen and in air for 24 hours.

Figure 4.18 presents the molar mass *versus* monomer conversion. The graph suggests during the induction period, no polymers chains were formed. Following this period, the effect of oxygen is overwritten, and oligomers are produced which propagate to form polymer chains. The reaction conducted in air reached low conversion, but the molar mass of the polymers remained high.

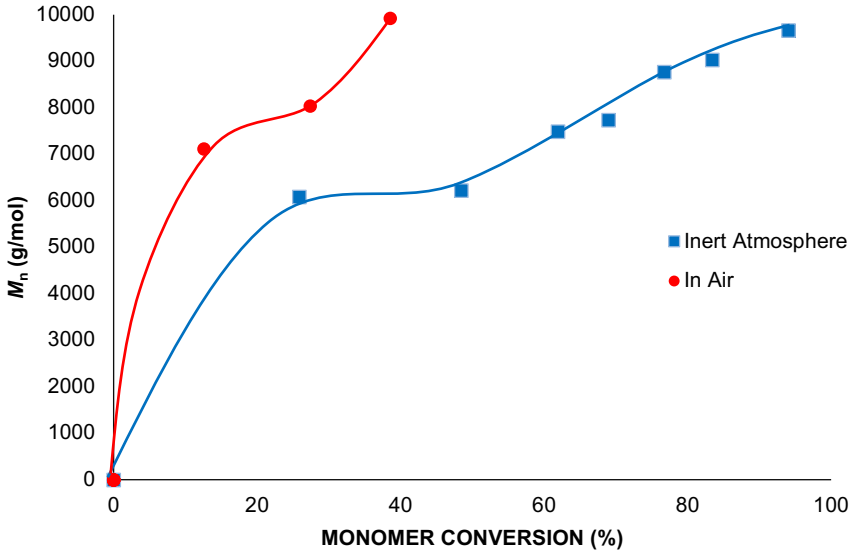


Figure 4.18. Molar mass (M_n) *versus* monomer conversion for the radical polymerisation of 5 g (50 mmol) MMA using 1.0 molar equivalents bromoform as a thermal imitator in 10 mL THF at 70 °C. The reactions were conducted under nitrogen and in air for 24 hours.

The semi-logarithmic plots, showing the first order dependence on monomer concentration, are given as Figure 4.19. The reactions show two-step linear progression for both experiments, indicating a change in radical concentration across time. For both reactions, a larger apparent rate constant is observed at the start of the reaction. For the reaction conducted under nitrogen, the k_{app} was calculated to be 0.300 h^{-1}. For the polymerisation conducted under oxygen the rate constant after the induction period was calculated to be equal to 0.160 h^{-1}. This suggests the presence of oxygen results in fewer radicals being released into the system. This is supported by articles, suggesting oxygen directly reacts with propagating chains and radicals.[113] For both reactions a second slower polymerisation regime is observed, which had a smaller apparent rate constant.

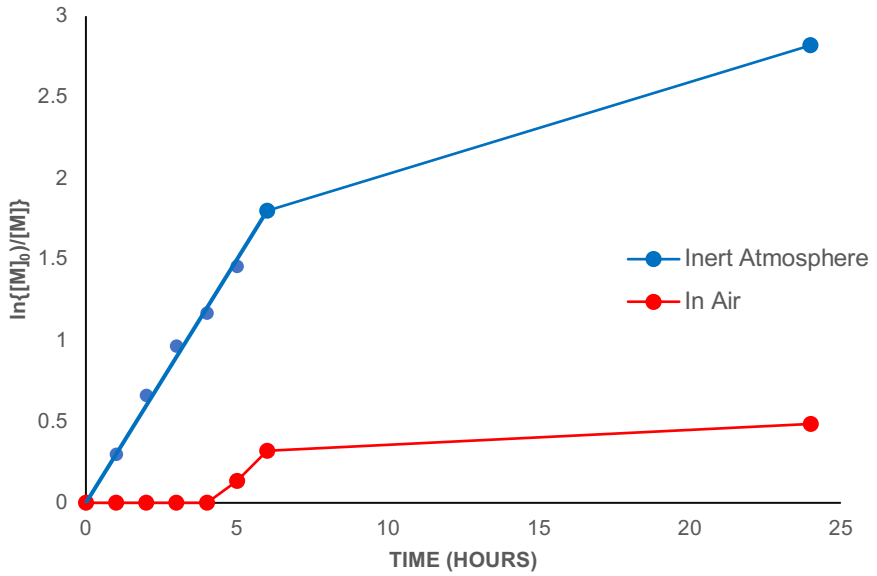


Figure 4.19. Semi-logarithmic plots for the radical polymerisation of 5 g (50 mmol) MMA using 1.0 molar equivalents bromoform as a thermal imitator in 10 mL THF at 70 °C. The reactions were conducted under nitrogen and in air for 24 hours.

4.3.2. The effect temperature has on the polymerisation of MMA using bromoform as a thermal initiator

Results from Section 4.3 showed bromoform can behave as a thermal initiator at 70 °C In THF, this was further investigated by conducting the reaction at different temperatures. For these reactions, 1 molar equivalents bromoform was used to polymerise 5 g (50 mmol) MMA in 10 mL THF. The reaction was conducted under nitrogen and the flask was placed in a preheated oil bath at temperatures ranging from 40-70 °C. Samples were taken every hour for the first 6 hours and one sample at 24 hours for kinetics studies. The molar mass and monomer conversion data for these reactions are shown in Table 4.4. The results show that bromoform can behave as an efficient thermal initiator at a range of temperatures. At temperatures above 60 °C, conversion above 77 % was achieved, but below this temperature, the conversion drops to less than 26 %. Table 4.4 shows increasing the temperature results in low molar mass polymers being formed which are closer to the target molar mass. The polymers produced at higher temperatures had lower dispersity compared to the reactions conducted at lower temperatures. Literature has suggested at lower temperatures, the termination mechanism for PMMA chains is primarily combination.[112].

Table 4.4. Molar mass data for the polymerisation of 5 g (50 mmol) MMA using 1 molar equivalents bromoform as a thermal imitator in 10 mL THF. The reactions were conducted at temperatures ranging from 40-70 °C for 24 hours.

Code	Reaction temperature (°C)	Monomer conversion (%) (a)	Observed M_n (g/mol) (b)	$Đ$ (b)	k_{app} (h^{-1}) ©
MOZ 16	70	94	9,700	1.55	0.300
MOZ 16A	60	77	15,000	1.68	0.179
MOZ 16B	50	26	24,000	1.82	0.044
MOZ 16C	40	22	30,000	1.89	0.014

(a) Monomer conversion determined by ^{1}H NMR spectroscopy

(b) M_n and $Đ$ determined by GPC [poly (methyl methacrylate) standards]

(c) The apparent rate constant (measured by ^{1}H NMR spectroscopy)

(d) Experiments were carried out once, due to limited time constraints.

The plots of monomer conversion *versus* time are shown in Figure 4.20 and molar mass *versus* time in Figure 4.21. Increasing the temperature results in high monomer conversion being achieved after 24 hours. Figure 4.20 shows a clear difference for monomer conversion progression for the reactions conducted above and below 50 °C. The monomer conversion is much slower for the reactions conducted below 50 °C, which could suggest at this temperature, not many molecules possess enough energy to overcome the activation energy. In radical polymerisation, this is normally the generation of the initiating radicals, in this case, the thermolysis of bromoform to cleave the Br radical. Figure 4.21 shows for the reaction conducted at 40 °C, molar mass increases rapidly after 2 hours compared to the reaction conducted at higher temperatures. This result suggests high molar mass polymers are produced early in the reaction at lower temperatures. Literature suggest termination via combination is favoured over disproportionation for MMA chains at lower temperatures.[114]

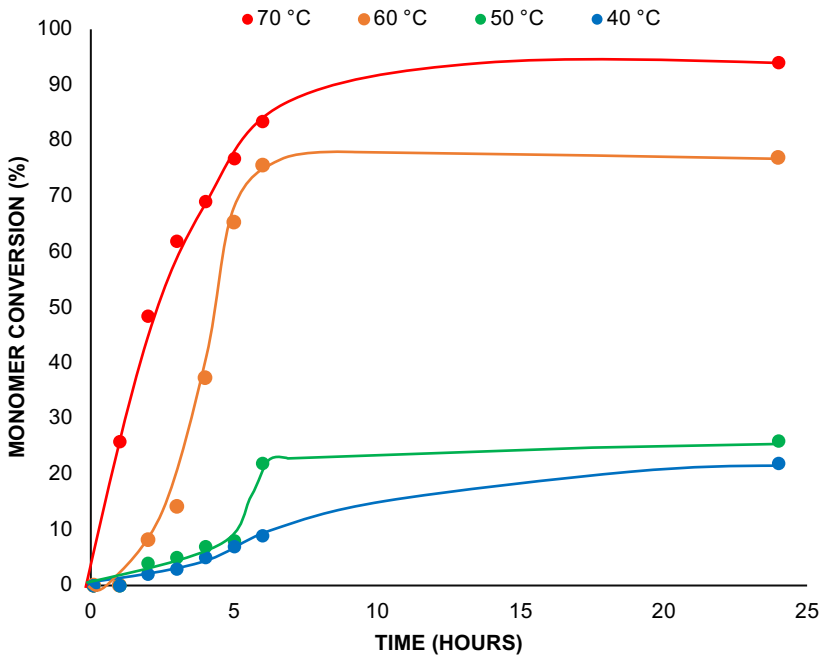


Figure 4.20. Monomer conversion *versus* time for the radical polymerisation of 5 g (50 mmol) MMA using 1.0 molar equivalents bromoform as a thermal imitator. The reactions were conducted in 10 mL THF at temperatures ranging from 40-70 °C for 24 hours.

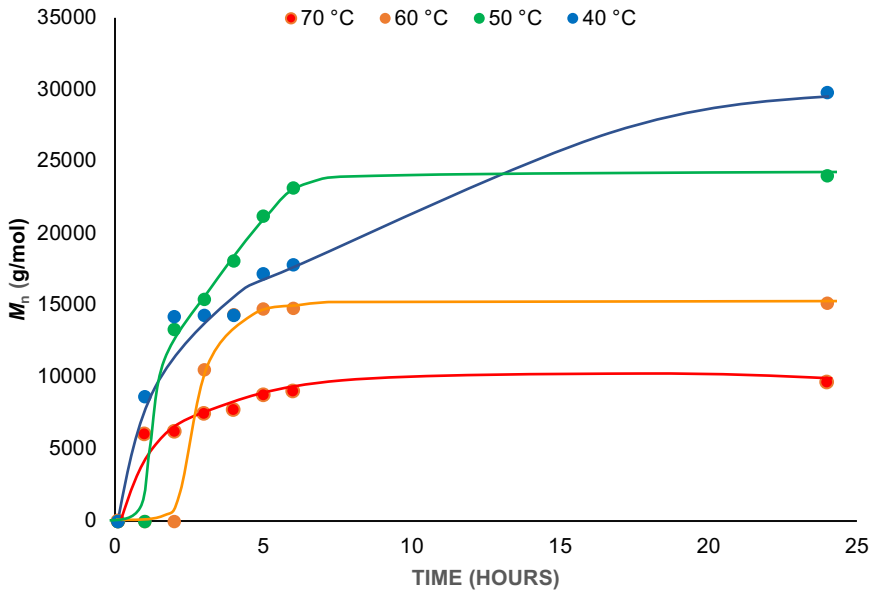


Figure 4.21. Molar mass (M_n) *versus* time for the radical polymerisation of 5 g (50 mmol) MMA using 1.0 molar equivalents bromoform as a thermal imitator. The reactions were conducted in 10 mL THF at temperatures ranging from 40-70 °C for 24 hours.

Figure 4.22 presents the molar mass *versus* monomer conversion for the following experiments. The graph shows 'high' molar mass polymers are obtained early in the reaction. Figure 4.22 shows for reactions conducted at 40 °C and 50 °C the molar mass increases rapidly at low conversion. This could suggest a termination reaction which results in the formation of high molar mass polymers. Figure 4.22 shows the reactions conducted at 60 °C and 70 °C, the molar mass increases gradually as conversion increases.

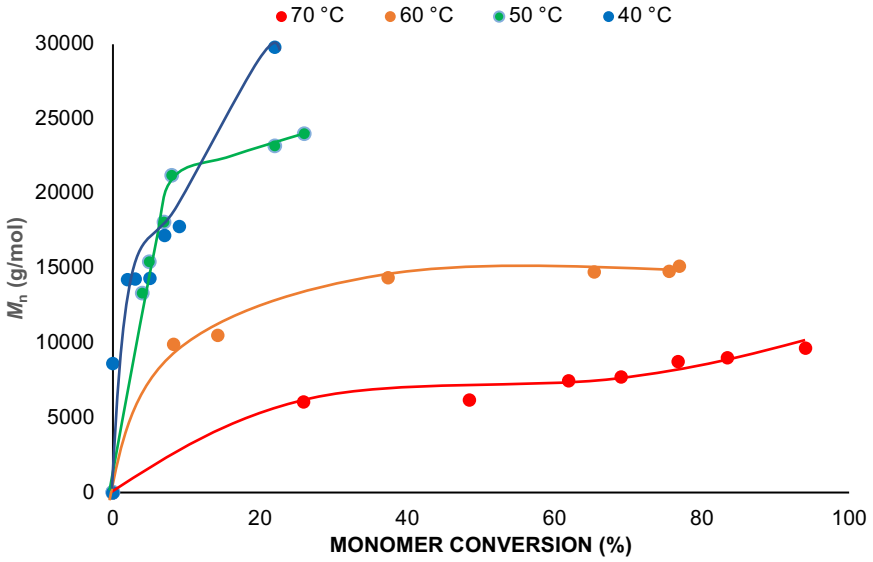


Figure 4.22. Molar mass (M_n) *versus* monomer conversion for the radical polymerisation of 5 g (50 mmol) MMA using 1.0 molar equivalents bromoform as a thermal imitator. The reactions were conducted in 10 mL THF at temperatures ranging from 40-70 °C for 24 hours.

The semi-logarithmic plots, showing the first order dependence on monomer concentration, are shown in Figure 4.23. Results from each reaction show two-step progression, indicating a change in radical concentration across time. Each reaction had a larger apparent rate constant at the start of the reaction. For the reaction conducted at 70 °C and 60 °C the k_{app} was equal to 0.300 h^{-1} and 0.179 h^{-1}, respectively. For the reactions at 50 °C and 40 °C, the apparent rate constant was equal to 0.044 h^{-1} and 0.014 h^{-1}, respectively. The results suggest at lower temperature the efficiency of bromoform as a thermal initiator decrease. Figure 4.23 suggests increasing the temperature results, in more radicals being released into the system. All reactions had a second slower polymerisation regime. The difference between the two regimes at 50 °C and 40 °C were not very significant.

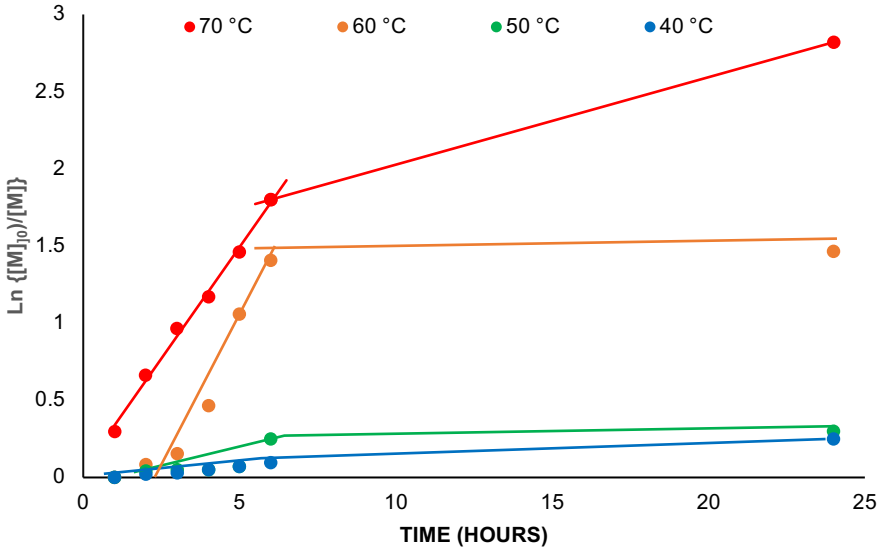


Figure 4.23. Semi-logarithmic plots for the radical polymerisation of 5 g (50 mmol) MMA using 1.*0* molar equivalents bromoform as a thermal imitator. The reactions were conducted in 10 mL THF at temperatures ranging from 40-70 °C for 24 hours.

The results from the pseudo-first order plots were used to calculate the activation energy from an Arrhenius plot. In 1889, Savante Arrhenius proposed the Arrhenius equation (Equation 4.1) which is based on the collision theory.[115]

$$k = Ae^{-\frac{E_a}{RT}} \qquad \text{(Equation 4.1)}$$

The Arrhenius equation is composed of a relationship between the rate constant, *k* against temperature, *T* in kelvin. E_a, is the minimum energy a molecule must possess to react to form a product in J mol^{-1}. The equation includes a pre-exponential factor, *A*, which takes into account the steric factor and the collision frequency and *R* refers to the ideal gas constant.

The Arrhenius equation can be rearranged to form an equation which can be used to determine the activation energy. For this equation the natural logarithm of each side is taken and rearranged in the form of *y=mx+c*. The linearised version of Arrhenius is shown in Equation 4.2.

$$\ln k = -\frac{E_a}{RT} + \ln A \qquad \text{(Equation 4.2)}$$

To calculate the activation energy the inverse of the temperature, in Kelvin is plot against the natural log of the rate constant. The gradient of the straight line is equal to $-E_a/R$ and the *y* intercept is equal to ln *A*. The apparent rate constant and the temperature used for the Arrhenius plot are shown in Table 4.5, including units coversion.

Table 4.5. Apparent rate constant and temperature unit conversions for Arrhenius plot for the preparation of PMMA using 1 molar equivalents bromoform as a thermal initiator. The reactions were conducted in 10 mL THF at temperatures ranging from 40-70 °C for 24 hours.

Temperature, *T* (°C)	**Temperature, *T* (K)**	**1/*T* (K^{-1})**	**Apparent rate constant, *k* (h^{-1})**	**Apparent rate constant, *k* (s^{-1})**	**ln *k***
40	313	0.0032	0.0139	50.0	3.9128
50	323	0.0031	0.0437	157.3	5.0583
60	333	0.0030	0.1785	642.6	6.4655
70	343	0.0029	0.3000	1080.0	6.9847

Figure 4.24 outlines the Arrhenius plot for the preparation of PMMA using 1 molar equivalents bromoform as an initiator. The graph shows the data points from the apparent rate constant fits the Arrhenius equation with a strong relationship. The gradient for the line was found to be equal to -11439, after multiplying by -*R*. The activation energy was found to be equal to 95103 J/mol, 95 kJ/mol. The *y*-intercept was found to be equal to 40.52, therefore the pre-exponential term is 3.95 $x10^{17}$ s^{-1}.

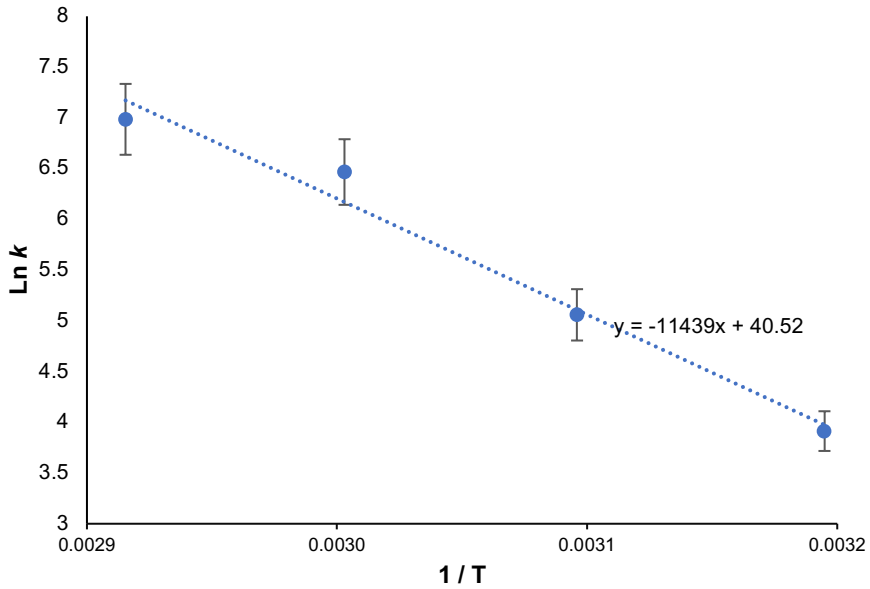
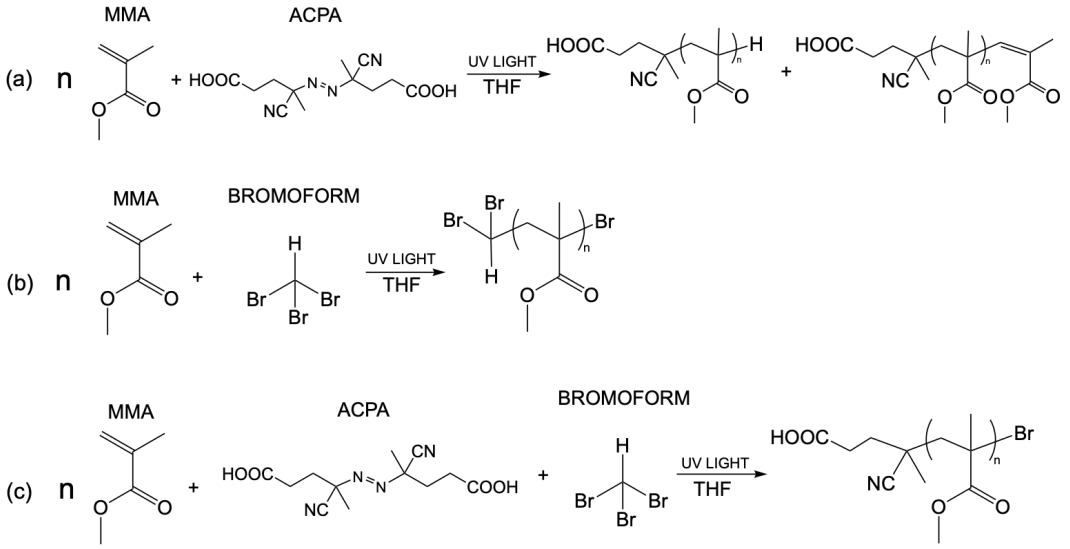


Figure 4.24. Arrhenius plot for the thermal polymerisation of MMA using 1.0 molar equivalents bromoform as a thermal initiator. The reaction was conducted in 10 mL THF at temperatures ranging from 40-70 °C for 24 hours.

The activation energy for the reaction using bromoform as a thermal initiator is smaller than the energy required for the thermal dissociation of AIBN, which has an activation energy equal to 130.1 $kJmol^{-1}$.[33] For radical polymerisation the rate of initiator decomposition is considered the rate determining step. From this, we could expect the activation energy for the radical polymerisation being close to this. The results from the Arrhenius plot, suggests that the activation energy for the polymerisation of MMA using bromoform as a thermal initiator could be lower than the activation of a normal conventional radical polymerisation, assuming the literature value for activation energy for the thermal dissociation of AIBN is the rate determining step. However, to make a direct comparison between the polymerisation of MMA using AIBN in THF, the experiment should be repeated at a series of different temperatures. This can be used to calculate the activation energy of the reaction and would be a better comparison to the polymerisation using bromoform as a thermal initiator.

4.4. THE EFFECT BROMOFORM HAS ON THE PHOTOPOLYMERISATION OF MMA

Following the preparation of PMMA under thermal conditions, the reactions were repeated at room temperature under UV light described in Section 2.2.5. The reactions conducted included the following: self-initiated polymerisation of MMA under UV light, a conventional radical polymerisation using ACPA as a photoinitiator and a series of polymerisation reaction where bromoform is added to the conventional radical polymerisation reaction. The reaction scheme for these experiments have been outlined in Scheme 4.2. The structure of the end groups have been outlined from the following assumptions: (a) MMA does not undergo self-initiated polymerisation, the reaction proceeds via termination by disproportionation (for convenience purpose), (b) bromoform behaves as a photoinitiator by the photolysis, both radicals produced can behave as the initiating radical and (c) bromoform behaves as a CTA which produces polymers with bromine end groupsl;.



Scheme 4.2. Synthesis of PMMA using: ACPA as a photo initiator (a), using bromoform as a photoinitiator (b), and bromoform as a CTA with ACPA (c). All reactions were conducted in 10 mL THF under UV light (λ = 100- 400 nm) for 6 hours. For simplicity only major products are shown.

The molar mass and monomer conversion data for these experiments have been outlined in Table 4.6. Conversions above 50 % was achieved for all reactions. The results suggest the addition of bromoform to the conventional radical polymerisation has a significant effect on the observed molar mass of the polymer and the conversion achieved after 6 hours. This is characteristic for the behaviour of bromoform behaving as a CTA which Thananukul *et.al* suggested for the photopolymerisation of acrylamides.[1] The results from this section and Section 3.3 suggest ACPA under the current conditions may not be an effective photoinitiator.

Table 4.6. Molar mass data for the polymerisation of 5 g (50 mmol) MMA using 0.2 molar equivalents ACPA with 0.1–2.0 molar equivalents bromoform in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

Code	Molar equivalents of bromoform added	Molar equivalents of ACPA added	Theoretical M_n (g/mol) (a)	Monomer conversion (%) (b)	Observed M_n (c) (g/mol)	$Đ$ (c)	k_{app} (h^{-1}) (d)
MOZ 20	0	0	-	-	-	-	-
MOZ 22	0	0.2	-	71	26,000	1.63	0.301
MOZ 24	0.1	0.2	40,000	69	26,000	1.55	0.216
MOZ 36	0.2	0.2	20,000	66	22,000	1.57	0.162
MOZ 25	0.5	0.2	8,000	66	18,000	1.61	0.199
MOZ 23	1.0	0.2	4,000	65	17,000	1.63	0.171
MOZ 26	2.0	0.2	2,000	51	11,000	1.48	0.124

(a) Molar equivalents of MMA = 40, theoretical M_n based on the assumption bromoform behaves as a CTA similar to a RAFT agent.

(b) Monomer conversion determined by ^{1}H NMR spectroscopy

(c) M_n and $Đ$ determined by GPC [poly(methyl methacrylate) standards]

(d) The apparent rate constant (measured by ^{1}H NMR spectroscopy)

(e) Experiments were carried out once, due to limited time constraints.

The kinetics for the reactions were followed by taking samples every hour. The reactions were stopped after 6 hours, due to laboratory working hours. The plots of monomer conversion *versus* time are shown in Figure 4.25 and molar mass *versus* time in Figure 4.26. Figure 4.25 shows the addition of bromoform results in low conversion being achieved after 6 hours. This is a similar trend to resultss in Section 3.3, for the photopolymerisation in styrene. The experiments conducted generally show, increasing the concentration of bromoform results in slower progression in monomer conversion. This trend is not followed by the experiments conducted using 0.2 and 0.5 molar equivalents bromoform, which may suggest the data contains anomalies. To identify the anomalies the experiments should be repeated. Figure 4.26 shows 'high' M_n polymers are achieved early in the reaction. The graph shows a clear difference between the observed molar mass for the reactions using ACPA only and the experiments containing bromoform.

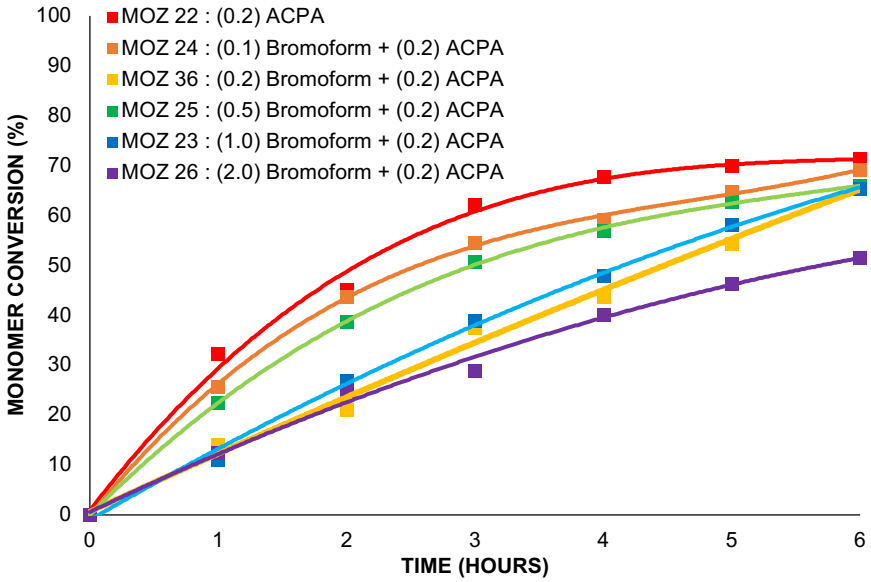


Figure 4.25. Monomer conversion *versus* time for the radical polymerisation of MMA using 0.2 molar equivalents ACPA and 0.1-2.0 molar equivalents bromoform in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

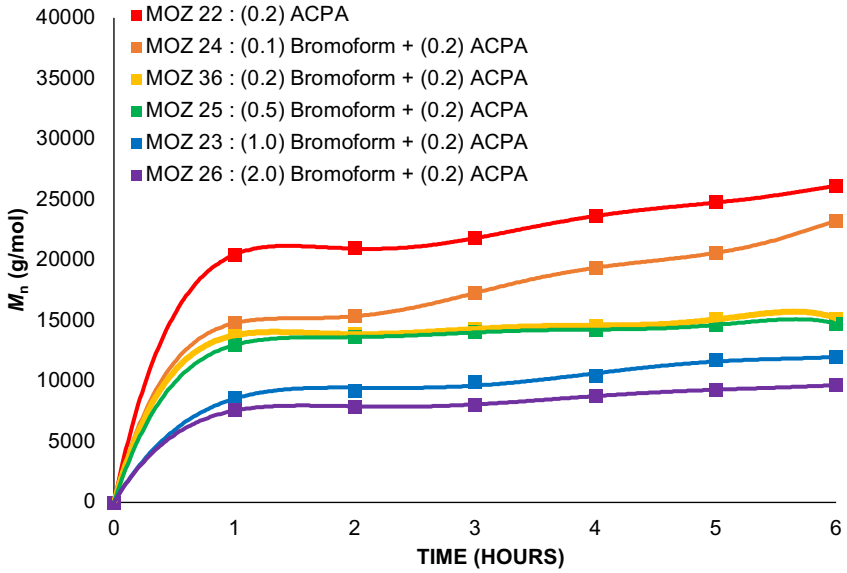


Figure 4.26. Molar mass (M_n) *versus* time for the radical polymerisation of MMA using 0.2 molar equivalents ACPA and 0.1-2.0 molar equivalents bromoform in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

Figure 4.27 shows the observed molar mass *versus* monomer conversion. The graph shows the addition of bromoform is hindering the production of high molar mass polymers and increasing the concentration has a greater effect on the observed molar mass. When the monomer conversions is above 60 %, a significant increase in molar mass is observed for the reactions using ACPA only and the reaction using 0.1 molar equivalents bromoform. This may suggest a termination reaction which leads to the production of 'high' molar mass polymers.

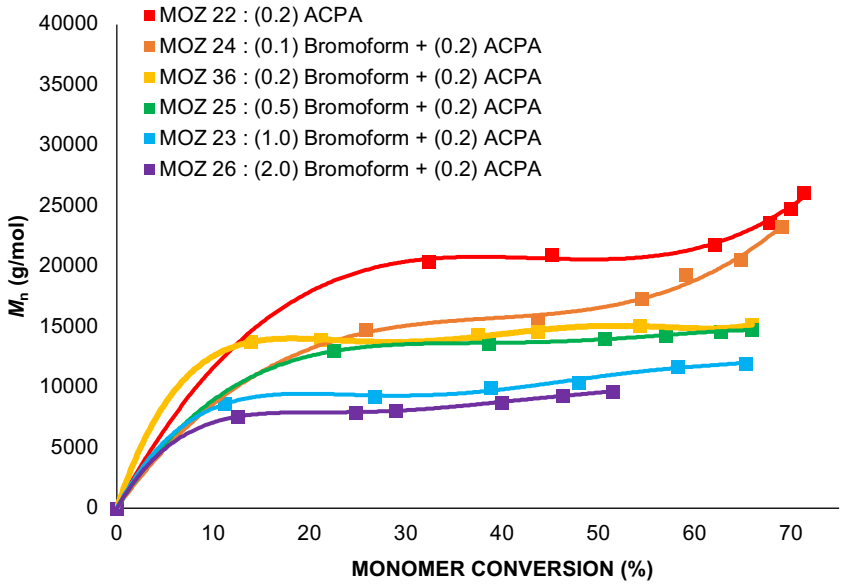


Figure 4.27. Molar mass (M_n) *versus* monomer conversion for the radical polymerisation of MMA using 0.2 molar equivalents ACPA and 0.1-2.0 molar equivalents bromoform in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

The semi-logarithmic plots, showing the first order dependence on monomer concentration are shown in Figure 4.28. For most experiments, a two-step progression is observed, which suggests a change in radical concentration. The conventional radical polymerisation initially had the largest apparent rate constant equal to 0.301 h^{-1}. The addition of bromoform to this system results in a smaller apparent rate constant being observed. Increasing the quantity of bromoform added has a significant effect on the observed for the apparent rate constant for the first regime. For the addition of 0.1 molar equivalents bromoform, a k_{app} equal to 0.216 h^{-1} is observed, whereas when 2.0 molar equivalents is added the k_{app} was equal to 0.124 h^{-1}. The trend between increasing the concentration, is not clear as the reactions using 0.2 molar and 0.5 molar equivalents bromoform does not follow this pattern. Furthermore, most reactions showed a second slower polymerisation regime which may suggest a termination step/reaction. This step is not present for the reactions, where 1.0 and 0.2 molar equivalents bromoform were used, instead, a second faster regime was observed. This suggests more radicals are present in the system during this stage, which could be explained by the Trosmordoff-Norrish effect, where the increase in viscosity leads to deviations in kinetic plots. The reaction conducted using 2.0 molar equivalents bromoform indicated a linear progression with a single apparent rate constant, which suggests a constant radical concentration. Most of these reactions didn't reach 'high' conversions, therefore it is difficult to identify if the radical concentration changed near the end of the reaction.

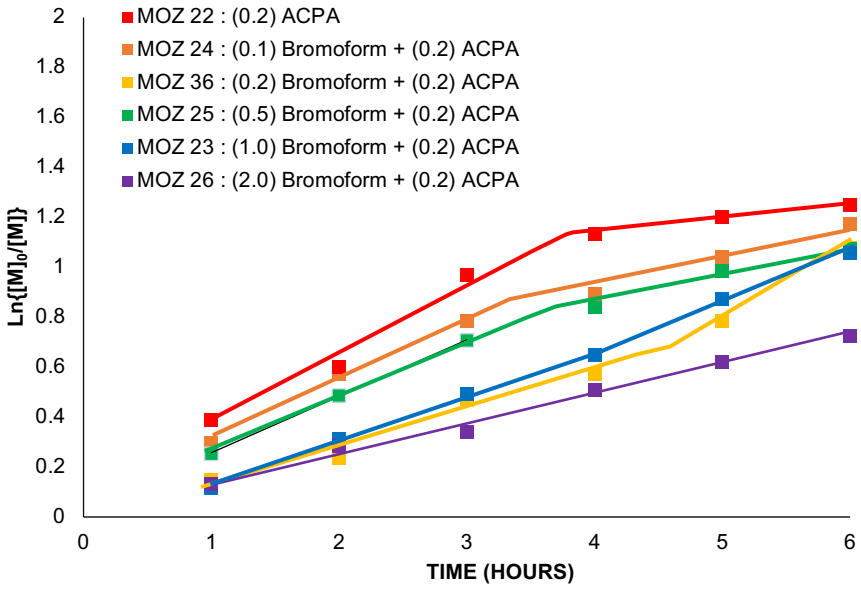


Figure 4.28. Semi-logarithmic plots for the radical polymerisation of MMA using 0.2 molar equivalents ACPA and 0.1-2.0 molar equivalents bromoform in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

4.4.1. Characterisation of PMMA prepared using bromoform under UV conditions

This section explains the results obtained from the characterisation of the polymers produced from the conventional radical polymerisation using ACPA and the reactions using 0.5 and 1.0 molar equivalents bromoform. The characterisation techniques used included the following: FTIR, DSC and NMR.

The FTIR for the polymers produced using the conventional radical polymerisation and using 0.5 and 1,0 molar equivalents bromoform are shown in Figure 4.29. The spectrum contains a strong C=O carbonyl stretch at 1730 cm^{-1}, O-CH_3 and C-O bending at 1250 cm^{-1}, and 1150 cm^{-1}. These bands are all characteristic for the ester group present in PMMA. The spectrum contains a series of C-H vibrations around 2995 cm^{-1} and 1400 cm^{-1} which are characteristic for the methyl and methylene stretch. The spectrum did not include any information on the end groups of the polymer, and all essentially look the same.

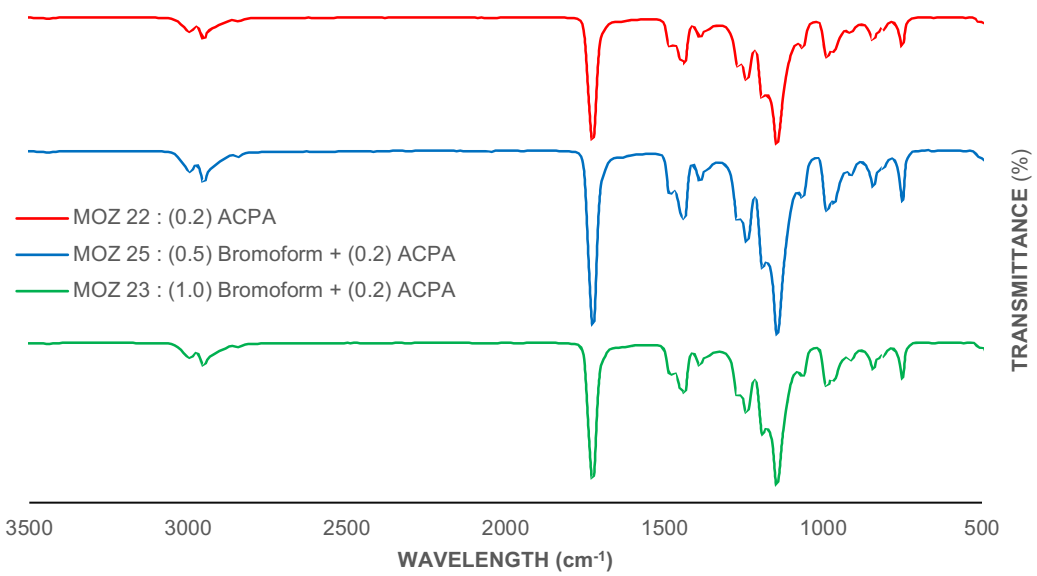


Figure 4.29. FTIR spectrum for the polymers produced from the radical polymerisation of MMA, using 0.2 molar equivalents ACPA and variable concentration of (0, 0.5, 1 molar equivalents) bromoform. The reactions were conducted in 10 mL THF under UV light (λ = 100-400 nm) for 6 hours.

DSC was used to determine the T_g for the resulting polymer produced. The thermograms are shown in Figure 4.30. It was found the polymers produced all showed one T_g, between 120-130 °C. Polymers produced using bromoform showed no significant change in polymer mechanical properties.

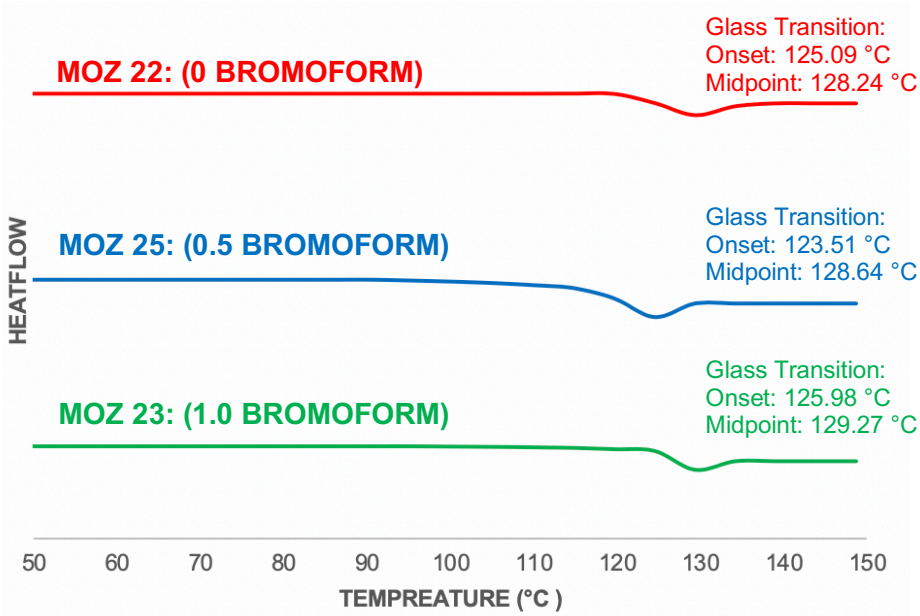


Figure 4.30. DSC thermogram for the final heating cycle for the polymer produced from the radical polymerisation of MMA, using 0.2 molar equivalents ACPA with (0, 0.5 and 1 molar equivalents) bromoform. There reactions were conducted in 10 mL THF under UV light (λ = 100-400 nm) for 6 hours.

Figure 4.31 outlines the ^{1}H NMR spectrum for the resulting polymers (in $CDCl_3$). ^{1}H NMR spectrum for the precipitated polymers (in $CDCl_3$) using 0, 0.5 and 1 molar equivalents bromoform in the radical polymerisation of MMA (*i.e.* with AIBN). The spectrum for the polymers contained 4 broad polymer resonance signals. The signal at 3.55 ppm is attributed to the methyl ester group of PMMA. The signal in the region ranging from 1.65 to 1.95 ppm and from 0.65 and 1.02 ppm are attributed to the methylene and methyl group of atactic PMMA, respectively. The spectrum for the polymers produced from the conventional radical polymerisation and using 1.0 molar equivalents bromoform contained a small signal at 3.45 ppm, is characteristic for residual THF.

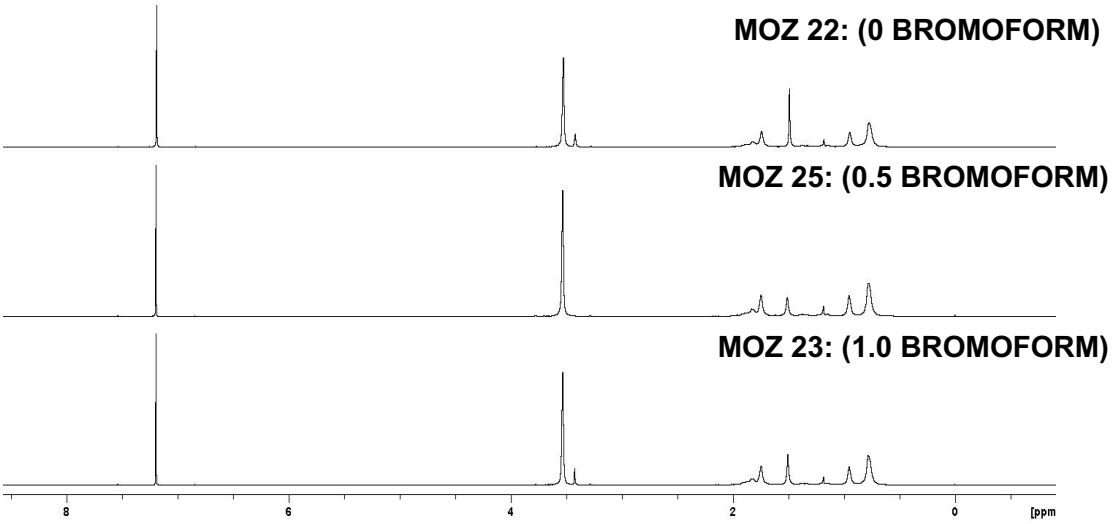


Figure 4.31 ^{1}H NMR spectrum (300 MHz) for the precipitated polymers produced from the radical polymerisation of MMA, using 41 mg (0.25 mmol) AIBN and variable concentration of (0, 0.5, 1 molar equivalents) bromoform. The reactions were conducted in 10 mL THF at 70 °C.

4.5. THE EFFECT ACPA HAS ON THE BROMOFORM-MEDIATED POLYMERISATION OF MMA UNDER UV CONDITIONS.

The results reported in Section 4.4 suggested bromoform offers some control over molar mass. In this section, a series of experiments were conducted using 1.0 molar equivalents bromoform with 0-1.0 molar equivalence ACPA to identify a reaction which offers the best control. The molar mass and monomer conversion data for these reactions are shown in Table 4.7. The results suggest under the current experimental conditions, bromoform does not behave as a photoinitiator for the photopolymerisation of MMA. This is a similar conclusion from Section 3.3 for the photopolymerisation of styrene. Both results counter Miller[2] suggestion of bromoform behaving as a photoinitiator. Table 4.7 shows increasing the concentration of ACPA, results in 'high' monomer conversion being achieved after 6 hours and low molar mass polymers being produced.

Table 4.7. Molar mass data for the polymerisation of 5 g (50 mmol) MMA using 1.0 molar equivalents bromoform with 0-1.0 molar equivalents ACPA in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

Code	Molar equivalents of ACPA added [(a)]	Monomer conversion (%) [(b)]	Observed M_n [(c)]	$Đ$ [(c)]	k_{app} (h^{-1}) [(d)]
MOZ 21	0	0	-	-	-
MOZ 27	0.1	50	11,600	1.54	0.097
MOZ 23	0.2	65	12,000	1.63	0.171
MOZ 28	0.5	72	10,000	1.75	0.194
MOZ 35	1.0	78	8,500	1.95	0.225

(a) Target degree of polymerisation DP= 40, M_n = 4,000 g/mol, assuming bromoform behaves as a CTA similar to RAFT polymerisation.

(b) Monomer conversion determined by ^{1}H NMR spectroscopy

(c) M_n and $Đ$ determined by GPC [poly(methyl methacrylate) standards]

(d) The apparent rate constant (measured by ^{1}H NMR spectroscopy)

(e) Experiments were carried out once, due to limited time constraints.

The kinetics for the reactions were followed by taking samples every hour. The reactions were stopped after 6 hours, due to laboratory working hours. The plots of monomer conversion *versus* time are shown in Figure 4.32 and molar mass *versus* time in Figure 4.33. Figure 4.32 shows increasing the concentration of ACPA results in high conversion being achieved earlier in the reaction. For example, when 1 molar equivalents ACPA is used 80 % monomer conversion is achieved within 6 hours, whereas when 0.1 molar equivalents ACPA is used only 50 % conversion was achieved. Figure 4.33 shows 'high' M_n polymers are achieved early in the reaction. The largest molar mass polymer obtained was for the reaction using 0.2 molar equivalents ACPA which slightly larger for the polymer obtained using 0.2 molar equivalents bromoform.

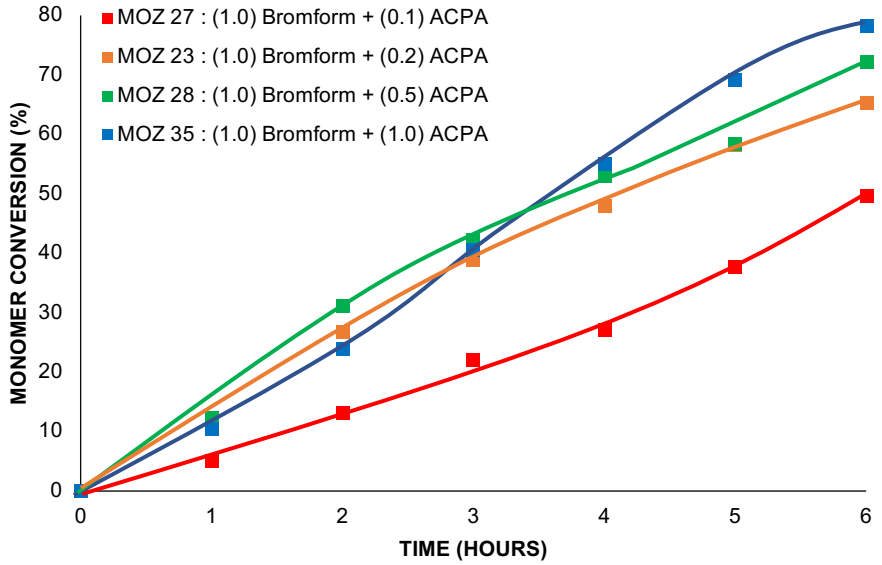


Figure 4.32. Monomer conversion *versus* time for the radical polymerisation of MMA using 1 molar equivalents bromoform and 0-1.0 molar equivalents ACPA in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

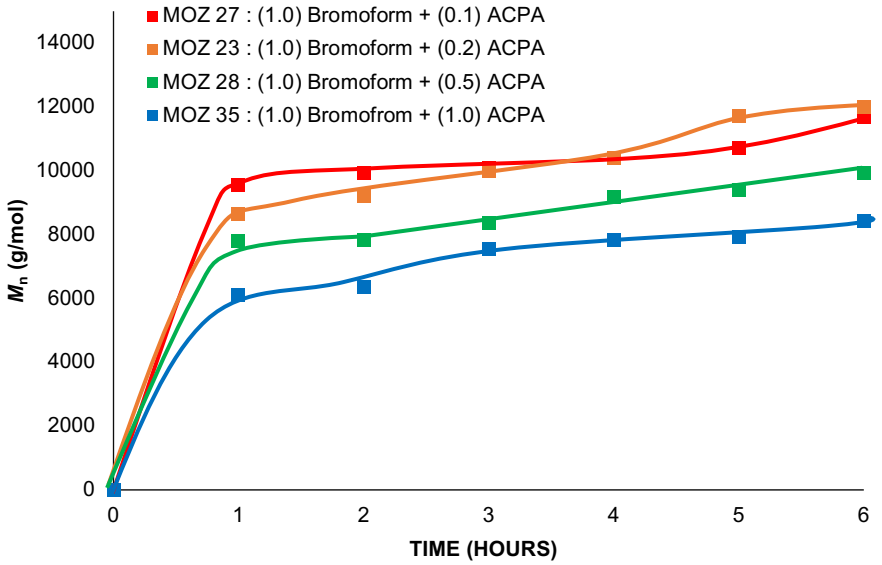


Figure 4.33. Molar mass (M_n) *versus* time for the radical polymerisation of MMA using 1 molar equivalents bromoform and 0-1.0molar equivalents ACPA in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

Figure 4.34 presents the molar mass versus monomer conversion. The graph shows a clear trend between, increasing the concentration of ACPA added and the conversion and molar mass obtained after 6 hours. Figure 4.34 shows the molar mass progression for the reaction using 0.1 molar equivalents ACPA was still gradually increasing, which may suggest if the reaction had reached high conversions, the molar mass may have been larger than what was initially observed.

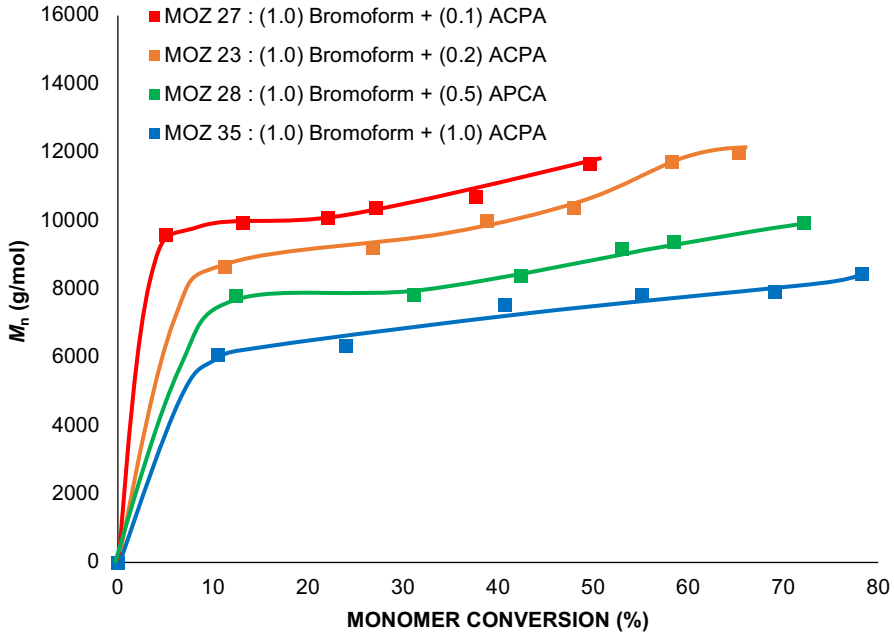


Figure 4.34. Molar mass (M_n) *versus* monomer conversion for the radical polymerisation of MMA using 1.0 molar equivalents bromoform and 0-1.0 molar equivalents ACPA in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

The semi-logarithmic plots, showing the first order dependence on monomer concentration, are given in Figure 4.35. Most experiments show two-step progression, indicating a change in radical concentration across time. The largest apparent rate constant was observed for the reaction which contained the most ACPA, as expected (k_{app} =0.225 h^{-1}). The smallest apparent rate constant was observed for the reaction which contained 0.1 molar equivalents ACPA (k_{app} = 0.097 h^{-1}). This result is expected as increasing the concentration of the initiator results in more radicals being released into the system. For the majority of experiments, a second faster polymerisation regime is observed. This suggests after a few hours, more radicals are released into the system. Results from these experiments are not conclusive due to high conversions not being reached for all experiments. Therefore, it is not possible to ascertain any deviations occur at higher conversions.

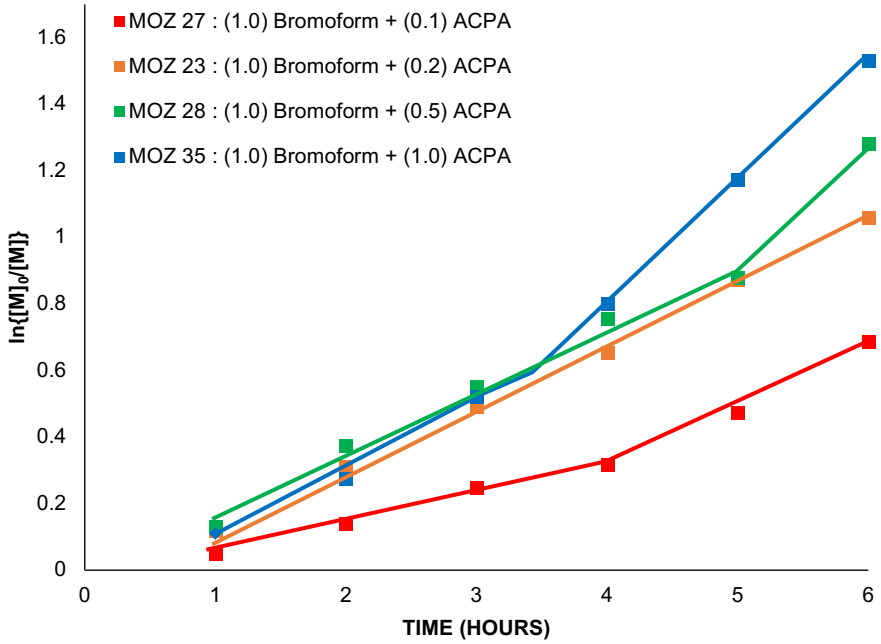


Figure 4.35. Semi-logarithmic plots for the radical polymerisation of MMA using 1.0 molar equivalents bromoform and 0-1.0 molar equivalents ACPA in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

An important factor to consider is the absorption of short-wave UV by the glass reaction flask, when explaining the photopolymerisation results. For example, the result from Figure 4.35 may have the signature of slow initiation + controlled polymerisation. This needs to be explored by conducting the reaction in quartz. Following the successful photopolymerisation of MMA, the effect the UV lamp had on the reaction temperatures was monitored. Section 4.3 suggested the temperature has a major effect on the behaviour of bromoform on the polymerisation. For this experiment, a temperatures probe was inserted into reaction flask for the photopolymerisation of MMA using 1 molar equivalents bromoform with 0.2 molar equivalents ACPA in 10 mL THF. The reactions was degassed and sealed with a rubber septum and placed under the UV lamp for 6 hours. The temperature was recorded every minute for 1 hour using a video recording, and then every 30 mins by monitoring the temperature on the thermometer. Figure 4.36 shows the change in temperatures of the reaction mixture during the 6 hours the UV lamp was on.

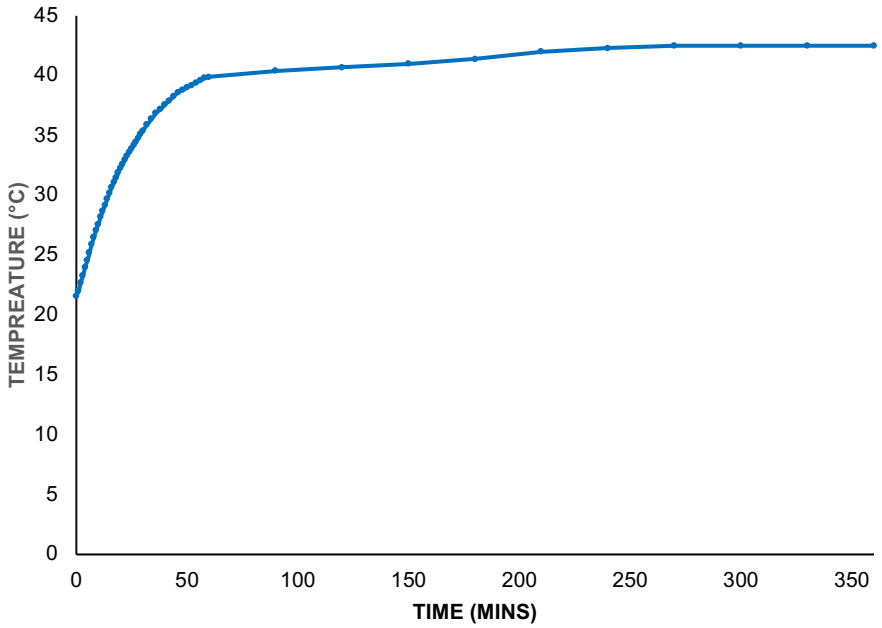


Figure 4.36. Temperature change for the photopolymerisation of 5 g (50 mmol) MMA using 1 molar equivalents bromoform and 0.2 molar equivalents ACPA in 10 mL THF. The reactions were conducted under UV light (λ = 100-400 nm) for 6 hours.

The graph shows the temperatures of the flask is initially at 21 °C and rapidly increases to 40 °C within 60 min. This indicates the UV lamp was heating the reaction flask, although the change in temperature could be explained by the exothermic behaviour of the radical polymerisation. Following the first hour, the temperatures remained constant around 42.5 for the rest of the experiment. This experiment is very useful when considering the termination reactions taking place between PMMA chains. The thermal stability of ACPA at elevated temperatures is very important in the current experimental setup. ACPA can behave as both a photoinitiator and a thermal initiator, ACPA has a 10-hour half-life at 68 °C, which is similar to AIBN.[33] The thermal stability of ACPA at 40 °C has not been explored, but there is a possibility that some thermal polymerisation could be taking place.

4.6. CONCLUSIONS

The results from this chapter show PMMA can be produced using the bromoform-mediated polymerisation under both thermal and UV conditions. The results from thermal polymerisation of MMA in Section 4.1 and 4.2 showed high conversions can be achieved within 24 hours and the technique offers some control over molar mass. The results from Section 4.3.2, showed bromoform can behave as a thermal initiator for the polymerisation of MMA in THF, at temperatures ranging from 40-70 °C. The results showed the reaction temperature has a major influence on the observed molar mass and the conversion reached after 24 hours. Conducting the polymerisation at lower temperatures results in high molar mass polymers being formed.

Results from Section 4.4 showed bromoform does not behave as a photo-initiator for the polymerisation of MMA in THF, this is the same conclusion made from Section 3.3 for the photopolymerisation of styrene under the same conditions. Section 4.4 showed the addition of bromoform to the radical polymerisation resulted in lower conversions being reached after 6 hours and ‘low’ molar mass polymer being obtained. Section 4.5 focused on identifying the best condition which offered the best control over molar mass and investigating the effect the UV lamp has on the reaction. The results showed from the experiments conducted, 1 molar equivalents bromoform with 1 molar ACPA reached the highest conversions and produced polymers with a molar mass close to the target molar mass, but with large dispersity. The investigation conducted on the effect the UV lamp had on the temperature, showed a significant increase for the first hour, from 21.5 °C to 40.5 °C. After this point, the temperature gradually increased to 42.5 °C for the next 5 hours. At this temperature, thermal polymerisation could be taking places due to ACPA and bromoform behaving as a thermal initiator at this temperature, this may complicate some of the obtained results.

Accordingly, Chapter 5 focuses on the preparation of block copolymers under thermal conditions using the homopolymers prepared from the bromoform-mediated polymerisation.

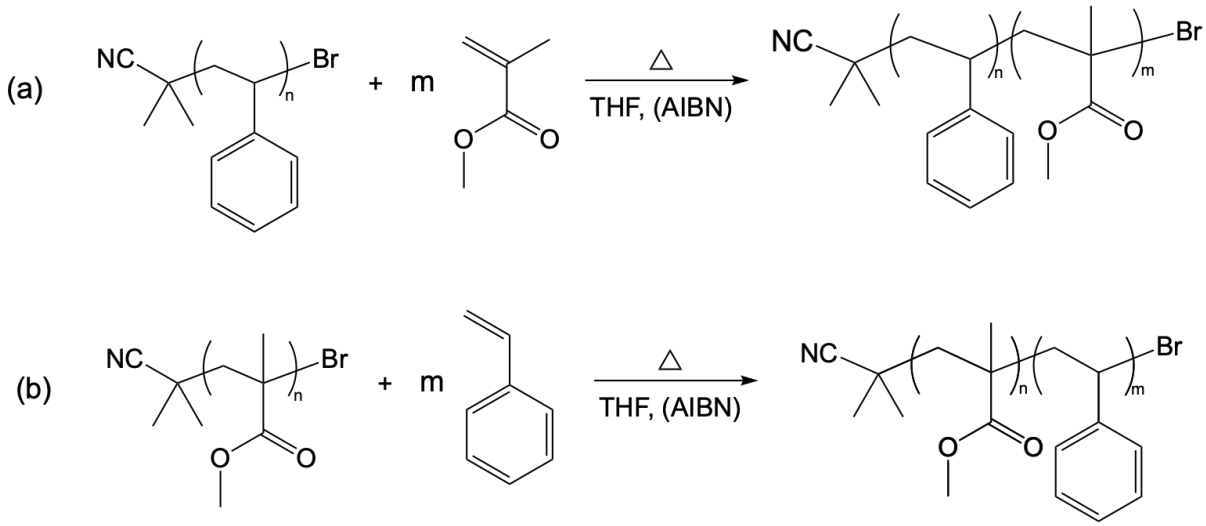
CHAPTER 5

PREPARATION OF BLOCK COPOLYMERS UNDER THERMAL CONDITION

5.1. PREPARATION OF PS-PMMA BLOCK COPOLYMERS

A variety of articles have suggested block copolymers (BCP) can be produced using homopolymers prepared from the haloalkanes. Miller[2] and Thananukul *et.al*[1] suggested polymers produced using bromoform possess labile end groups, that can be reinitiated to start the polymerisation of a second monomer under UV light. Dunn *et.al* [85] noticed a similar trend with the polymers prepared using carbon tetrabromide and bromotrichloromethane as transfer agents. Dunn *et.al* suggested PS prepared using these transfer agents possessed terminal C-Br bonds which could dissociate to form PS and bromine radicals. Dunn *et.al* suggested both radicals can initiate the polymerisation of the second monomer to produce a mixture of products. These being the BCPs formed from the PS radical, PMMA homopolymer and residual PS.

The results reported in Chapters 3 and 4 suggest PS and PMMA can be prepared using bromoform-mediated polymerisation. Results from Section 4.3.2 suggested bromoform can behave as a thermal initiator for the polymerisation of MMA. However, the results for the polymerisation of styrene under the same conditions were not clear enough. Due to this uncertainty, the polymers prepared using 1 molar equivalents bromoform with 0.2 molar equivalent, AIBN were used for block copolymer synthesis. The designed experiments included the following: using PS as a possible macro-initiator for the polymerisation of MMA and using PMMA for the polymerisation of styrene. In each experiment AIBN was added to identify if the homopolymer behaved as a macro-CTA. For these experiments the target was to prepare 1 g block copolymer, in 5 mL THF (20 wt%). Kinetic studies were conducted on all experiments, by taking samples every hour for the first 6 hours and a final sample at 24 hours. The samples were used to monitor the monomer conversion and molar mass progression using ^{1}H NMR spectroscopy and GPC, respectively. The reaction scheme for these experiments is shown in Scheme 5.1. The following assumptions were made when outlining the structure of the polymer end groups: The polymers prepared using the bromoform-mediated polymerisation possess C-Br terminal end groups, which can be reinitiated by thermal decomposition to form macro-radicals and bromine radicals. Ideally, the homopolymer radical formed reacts primarily with the 2nd monomer to form the block copolymers instead of recombining to form its homopolymer.



Scheme 5.1. Synthesis of PS-*b*-PMMA block copolymer using PS (M_n = 9,600 g/mol), MMA with and without the addition of AIBN in 5 mL THF at 70 °C for 24 hours (a). Synthesis of PMMA-*b*-PS block copolymer using PMMA (M_n= 24,000 g/mol), styrene with and without the addition of AIBN (b). Both experiments were conducted in 5 mL THF at 70 °C for 24 hours. For simplicity only major products are shown.

5.2. Synthesis of PS-*b*-PMMA using PS as a macro-initiator

For the preparation of PS-*b*-PMMA, PS homopolymer (M_n = 9,600 g/mol, $Đ$ = 1.34), prepared from the thermal polymerisation of styrene using bromoform was used as a CTA and AIBN with a molar ratio of 1:0.2. The progression of molar mass and monomer conversion for the following experiment are shown in Table 5.1. The results show after 6 hours, 91 % monomer conversion is achieved. The molar mass data show that as the reaction proceeds the observed molar mass of the polymers decreases and the dispersity increases. The polymer obtained from precipitation had a smaller M_n and a larger dispersity compared to the PS homopolymer used.

Table 5.1. Molar mass and monomer conversion data from the kinetic samples taken for the preparation of 1 g PS-*b*-PMMA using 502 mg (0.05 mmol) PS (M_n = 9,600 g/mol, $Đ$ = 1.34) as a macro-initiator and 482 mg (4.81 mmol) MMA. The reactions were conducted in 5 mL THF at 70 °C for 24 hours.

Time (Hours)	Monomer Conversion (%) [(a)]	Observed M_n (g/mol) [(b)]	$Đ$ [(b)]
1	20	7,300	2.05
2	49	7,000	2.27
3	75	6,900	2.27
4	78	6,500	2.36
5	84	5,700	2.55
6	91	6,000	2.47
24	98	6,400	2.39
FINAL [(c)]	-	9,200	1.73

(a) Monomer conversion determined by ^{1}H NMR spectroscopy

(b) M_n and $Đ$ determined by GPC [poly(methyl methacrylate) standards]

(c) Final polymers were extracted using precipitation in methanol

The NMR for the precipitated product in $CDCl_3$ is presented in Figure 5.1. The resonance signal at 3.55 ppm is attributed to the methyl ester group of PMMA. The signals in the region ranging from 1.65 to 1.95 ppm and from 0.65 and 1.02 ppm are attributed to the methylene and methyl group of atactic PMMA, respectively. The two resonance signals in the region of 7.56 ppm and 6.25 ppm are characteristic of benzyl protons and the resonance signals around 2.23 ppm represents methylene protons characteristic for PS.

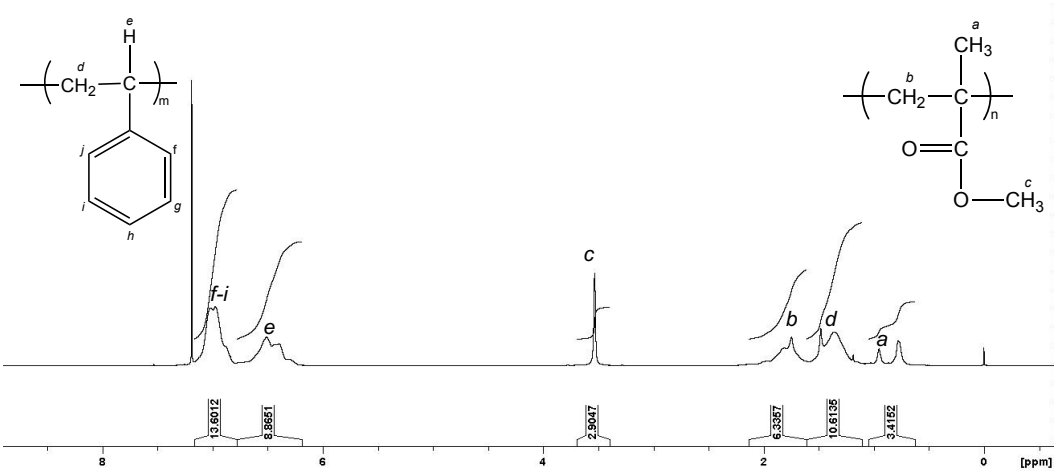


Figure 5.1. ^{1}H NMR spectra for the precipitated polymer produced from the polymerisation of 482 mg (4.81 mmol) MMA using 502 mg (0.05 mmol) PS as a macro-initiator. The reaction was conducted in 5 mL THF at 70 °C for 24 hours. Chemical structure of PMMA is shown at the top-right and PS at the top-left. The resonance labelled with low case letter are assigned to each particular chemical group.

To investigate if a block copolymer had been formed, the GPC trace for the kinetic samples were examined. If the homopolymer behaved as a macro-initiator we would expect the second monomer unit to add onto the chain and the polymer molar mass to increase. As a result of chain lengths increasing, the retention time for the polymer chain would increase and the curves would shift to shorter retention times. Figure 5.2 shows the GPC traces for the kinetic samples taken for the reaction where PS is used as a macroinitiator.

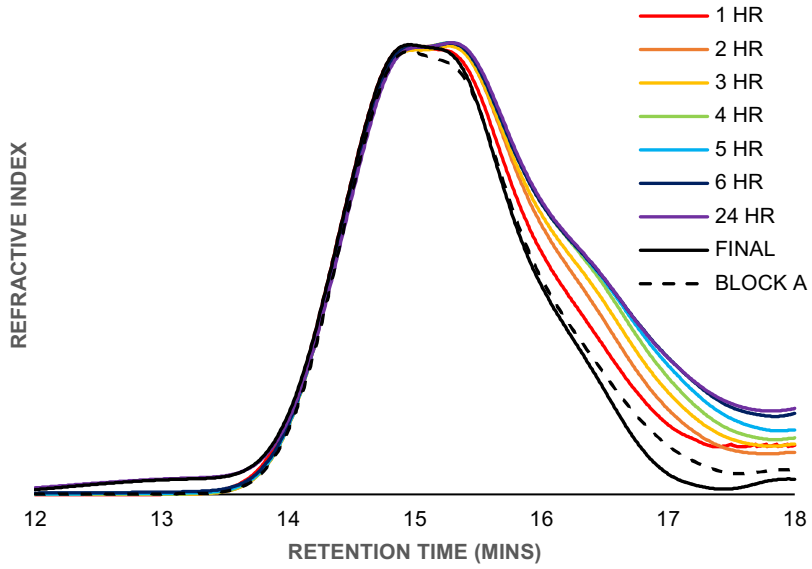


Figure 5.2. GPC traces for the kinetic samples taken for the preparation of PS-*b*-PMMA using 502 mg (0.05 mmol) PS as a macro-initiator and 482 mg (4.81 mmol) MMA. The reaction was conducted in 5 mL THF at 70 °C across 24 hours.

Figure 5.2 shows no change in retention time for the trace of each kinetic sample. This suggests the length of the polymer chains has not changed. Figure 5.2 shows the appearance of a shoulder on each curve. The evidence from the ^{1}H NMR and the GPC traces show monomer units are being converted into PMMA homopolymer. Results from GPC traces shows the intensity of the shoulder increases as a result of low molar mass PMMA being formed. The GPC trace for the polymer obtained from precipitation shows the disappearance of the shoulder peak, which suggests some PMMA was removed.

To investigate further an FTIR of the precipitated polymer was performed to identify the main functional groups present. Figure 5.3 shows the FTIR spectra for the resulting polymer. The stretching around 3000 cm^{-1} and 700 cm^{-1} are characteristic for the C-H bond in monosubstituted benzene. The spectrum contains stretches resembling the functional groups of PMMA such as, a strong C=O carbonyl stretch at 1730 cm^{-1}, O-CH_3 stretch at 1250 cm^{-1}, and C-O bending at 1150 cm^{-1}. The following stretches suggest the presence of an ester group in the sample from PMMA.

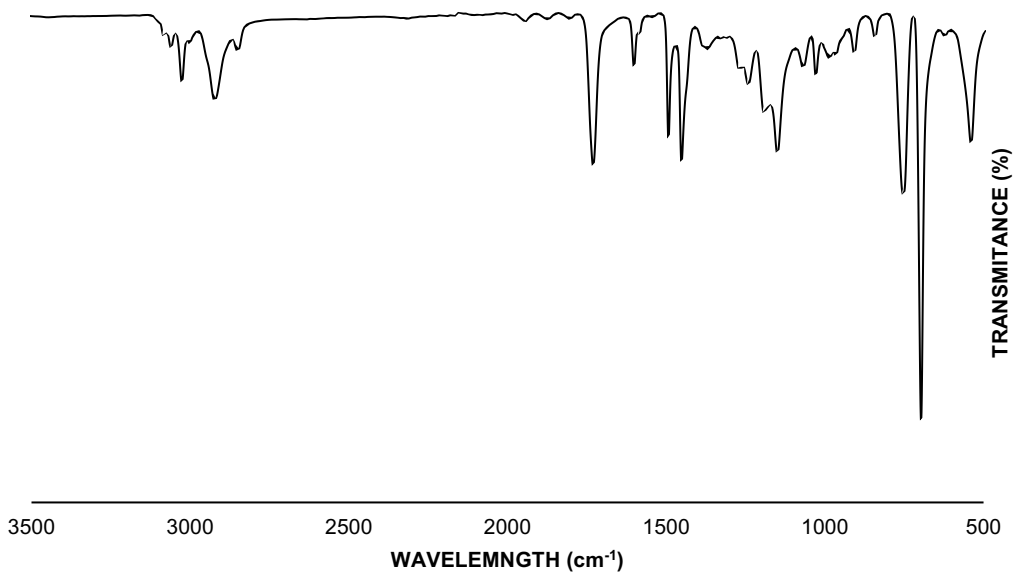


Figure 5.3. FTIR spectrum for the precipitated polymer obtained from the polymerisation of 482 mg (4.81 mmol) MMA using 502 mg (0.05 mmol) PS as a macro-initiator. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

To analyse the mechanical properties of the final polymer, the T_g was determined using DSC. The thermogram for the precipitated polymer is show in Figure 5.4. The DSC thermogram outlines two glass transition, the first one occurs around 95 °C and a small transition is observed around 116 °C. The low temperature transition is characteristic for PS,[116] while the high temperature transition is characteristic of PMMA.[108] The transition is minimal, which suggests a small quantity of PMMA is present.

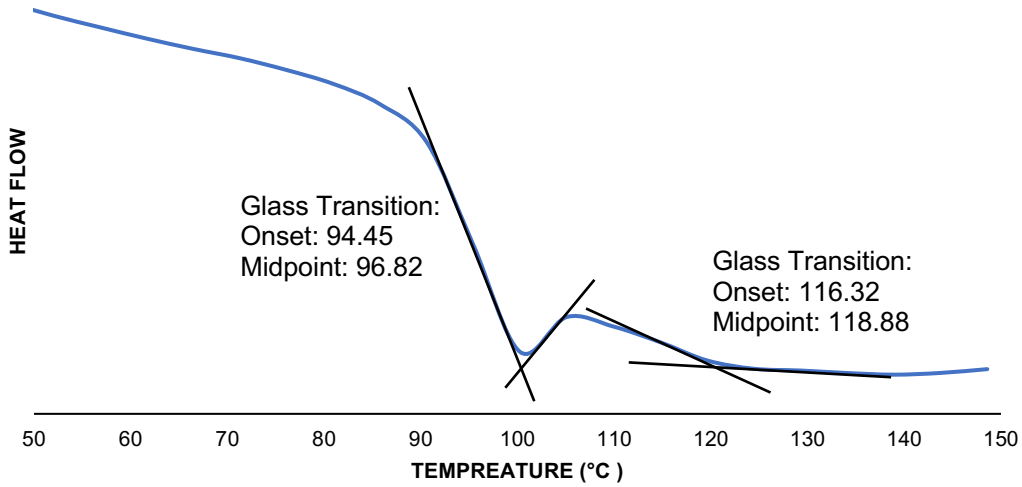


Figure 5.4. DSC thermogram for the precipitated polymer produced from the polymerisation of 482 mg (4.81 mmol) MMA using 502 mg (0.05 mmol) PS as a macro-initiator. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

5.3. Synthesis of PS-*b*-PMMA using PS as a macro-CTA

The experiment was then repeated with the addition of 1.70 mg (0.01 mmol) AIBN. For this reaction, PS homopolymer prepared using bromoform is assumed to behave as a macro-CTA. The molar mass and monomer conversion data for the kinetic samples taken are shown in Table 5.2. The results show after 24 hours, 98 % conversion was achieved. The polymer obtained from precipitation had a smaller M_n and a larger dispersity compared to the starting PS homopolymer.

Table 5.2. Molar mass and monomer conversion data from the kinetic samples taken for the preparation of PS-*b*-PMMA using 502 mg (0.05 mmol) PS (M_n = 9,600 g/mol, $Đ$ = 1.34) as a macro-initiator, 482 mg (4.81 mmol) MMA and 0.2 molar equivalents AIBN. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

Time (Hours)	Monomer Conversion (%) [(a)]	Observed M_n (g/mol) [(b)]	$Đ$ [(b)]
1	36	11,100	1.31
2	43	9,200	1.79
3	52	8,800	1.64
4	58	8,600	1.72
5	67	8,300	1.74
6	78	7,400	1.85
24	98	7,700	1.82
FINAL [(c)]	-	8,400	1.77

(a) Monomer conversion determined by ^{1}H NMR spectroscopy

(b) M_n and $Đ$ determined by GPC [poly(methyl methacrylate) standards]

(c) Final polymer was isolated by precipitation in methanol

The NMR for the precipitated polymer in $CDCl_3$ is presented in Figure 5.5. The resonance signal at 3.55 ppm is attributed to the methyl ester group of PMMA. The signals in the region ranging from 1.65 to 1.95 ppm and from 0.65 and 1.02 ppm are attributed to the methylene and methyl group of atactic PMMA, respectively. The two resonance signals in the region of 7.56 ppm and 6.25 ppm are characteristic of benzyl protons and the resonance signals around 2.23 ppm represents methylene protons characteristic for PS.

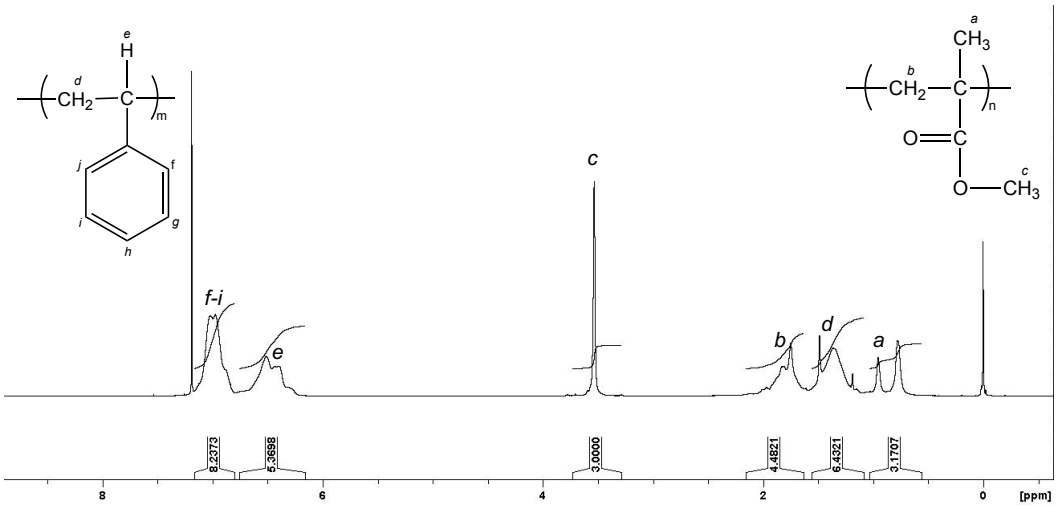


Figure 5.5. ^{1}H NMR spectra for the precipitated polymer produced from the polymerisation of 482 mg (4.81 mmol) MMA using 502 mg (0.05 mmol) PS as a macro-CTA and 0.2 molar equivalents AIBN. The reaction was conducted in 5 mL THF at 70 °C for 24 hours. Chemical structure of PMMA is shown in the top-right and PS at the top-left. The resonance labelled with low case letter are assigned to each particular chemical group.

Figure 5.6 outlines the GPC trace for the kinetic samples taken for the following experiement. The GPC traces show no change in retention time which suggests the chain length has not increased. Figure 5.6 shows as the reaction proceeds, a shoulder on each curve is observed. This implies the production of short chain polymers. Using the information obtained from the ^{1}H NMR this would be low molar mass PMMA. The GPC trace for the polymer obtained from precipitation shows the shoulder has decreased, which suggests some PMMA chains was removed.

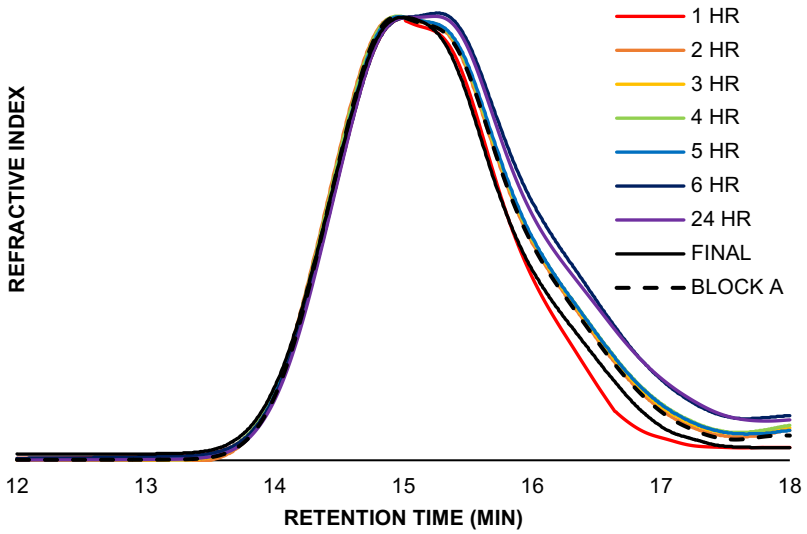


Figure 5.6. GPC traces for the kinetic samples taken for the preparation of PS-*b*-PMMA using 502 mg (0.05 mmol) PS as a macro-CTA, 482 mg (4.81 mmol) MMA and 0.2 molar equivalents AIBN. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

Figure 5.7 shows the FTIR spectrum for the precipitated polymer. The stretching around 700 cm^{-1} is characteristic for the C-H bond in monosubstituted benzene. The spectrum contains stretches resembling the functional groups of PMMA such as, a strong C=O carbonyl stretch at 1730 cm^{-1}, O-CH_3 stretch at 1250 cm^{-1}, and C-O bending at 1150 cm^{-1}. The stretches suggest the presence of an ester group in the final product.

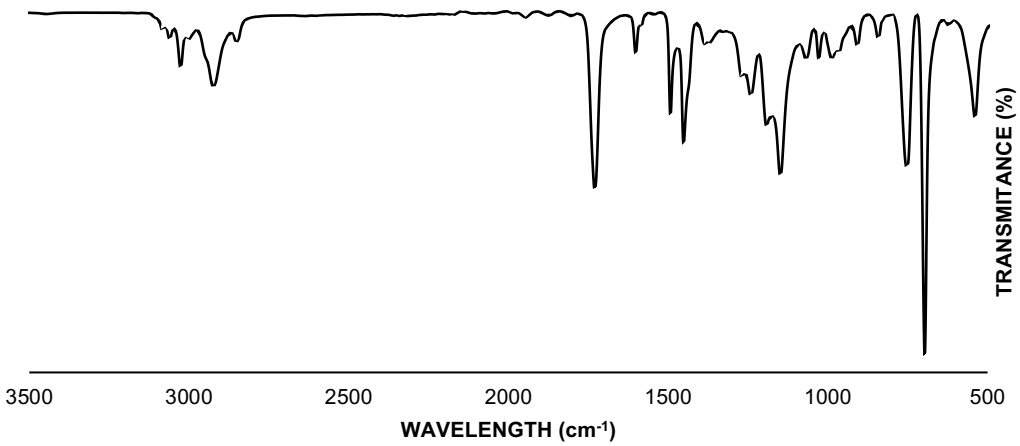


Figure 5.7. FTIR spectrum for the precipitated polymer produced from the polymerisation of 482 mg (4.81 mmol) MMA using 502 mg (0.05 mmol) PS as a macro-CTA and 0.2 molar equivalents AIBN. 1 conducted in 5 mL THF at 70 °C for 24 hours.

The DSC thermogram for the precipitated polymer is shown in Figure 5.8. The thermogram outlines two glass transitions, a large transition around 97 °C which is characteristic for PS and a small transition around 120 °C which is characteristic for PMMA. The low temperature transition is much larger compared to the transition observed in Figure 5.4, for the reaction where no AIBN was added. This could suggest the addition of AIBN has resulted in PMMA homopolymer being produced over the block copolymer.

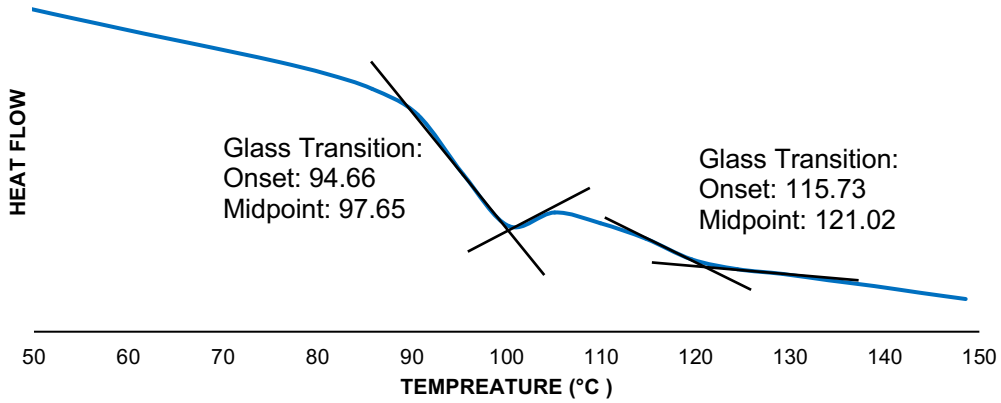


Figure 5.8. DSC thermogram for the precipitated polymer from the polymerisation of 482 mg (4.81 mmol) MMA using 502 mg (0.05 mmol) PS as a macro-CTA and 1.70 mg (0.01 mmol) AIBN. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

The results from ^{1}H NMR, FTIR and DSC suggest the production PMMA homopolymer. The GPC data shows that the length of the polymer chain has not increased. The molar mass data for the precipitated polymrt had a larger dispersity compared to the starting material, which shows the production of low molar mass PMMA. When comparing the results from Sections 5.2 to 5.3, the addition of AIBN has most likely resulted in the radical polymerisation of MMA, where PMMA homopolymer is primarily formed.

5.4. PREPARATION OF PMMA-*b*-PS USING PMMA AS A MACRO-INITIATOR

The PMMA homopolymer (M_n = 24,000 g/mol, $Đ$ = 1.56) prepared from the thermal polymerisation of MMA, using 0.2 molar equivalents AIBN with 1 molar equivalents bromoform was used as the starting block. The progression of molar mass and monomer conversion for this experiment is shown in Table 5.3. The results show a linear progression in monomer conversion and 87 % monomer conversion being achieved within 6 hours. The molar mass data shows a linear increase in observed molar mass for the duration of the reaction, which suggests an increase in polymer chain length. In general, the dispersity increases gradually for the duration of the polymerisation. After 24 hours the polymer was isolated by precipitation in methanol.

Table 5.3. Molar mass and monomer conversion data from the kinetic samples taken for the preparation of 1 g PMMA-*b*-PS using 501 mg (0.05 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator and 522 mg (4.80 mmol) styrene. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

Time (Hours)	Monomer Conversion (%) [(a)]	Observed M_n (g/mol) [(b)]	$Đ$ [(b)]
1	34	19,800	1.32
2	55	23,700	1.41
3	64	25,100	1.34
4	68	30,000	1.44
5	79	31,000	1.58
6	87	45,700	1.76
24	98	53,000	2.51
FINAL [(c)]	-	54,000	2.41

(a) Monomer conversion determined by ^{1}H NMR spectroscopy

(b) M_n and $Đ$ determined by GPC [polystyrene standards]

(c) Final polymer was isolated by precipitation in methanol

The ^{1}H NMR for the precipitated product in $CDCl_3$ is shown in Figure 5.9 The resonance signal at 3.55 ppm is attributed to the methyl ester group of PMMA. The signals in the region ranging from 1.65 to 1.95 ppm and from 0.65 and 1.02 ppm are attributed to the methylene and methyl group of atactic PMMA, respectively. The two resonance signals in the region of 7.56 ppm and 6.25 ppm are characteristic of benzyl protons and the resonance signals around 2.23 ppm represents methylene protons characteristic for PS. The integrals of the polymer protons were used to calculate the actual ratio of each monomer unit present in the copolymer. The actual ratio was calculated to be equal to 50:170. Which is significantly larger than the target ratio, which may suggest the presence of PS homopolymer in the final product.

Integrals of PMMA protons: Integral of PS protons 3/3:16.89/5 1: 3.4 50:170

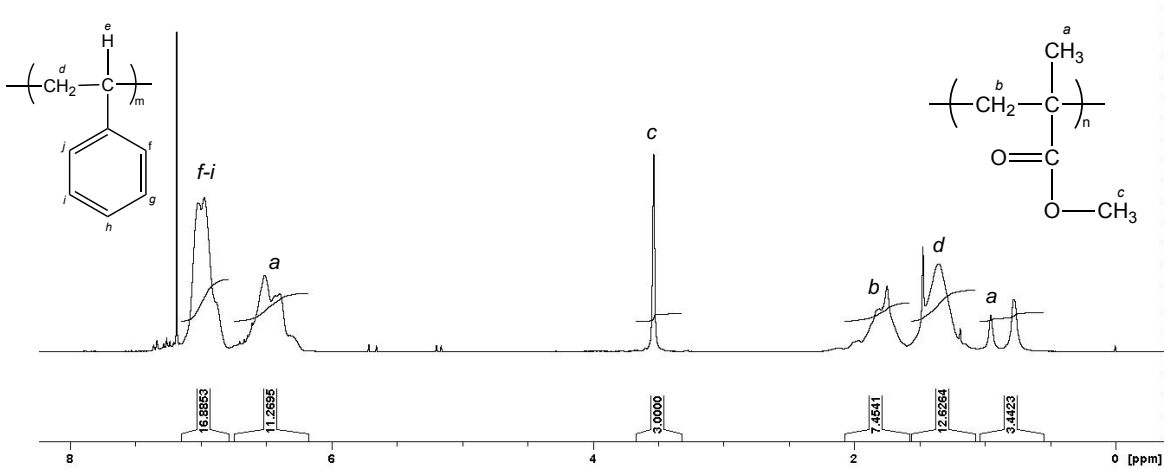


Figure 5.9. ^{1}H NMR spectra (300 MHz) for the precipitated polymer produced from the preparation of PMMA-*b*-PS, using PMMA as a macro-initiator. Chemical structure of PMMA is shown at the top-right and PS at the top-left. The resonance labelled with low case letter are assigned to each particular chemical group.

Figure 5.10 outlines the GPC traces for the kinetic samples taken. The GPC traces shows a clear change in retention time for the kinetic samples taken. The GPC trace suggests the length of the polymer chain is increasing. Using the evidence from ^{1}H NMR we can assume the styrene monomers are sequentially adding onto the PMMA block. Figure 5.10 shows the production of a shoulder on most traces, which is clearly visible for the GPC trace at 24 hours. The GPC trace for the final polymer shows After precipitation, the side product is removed.

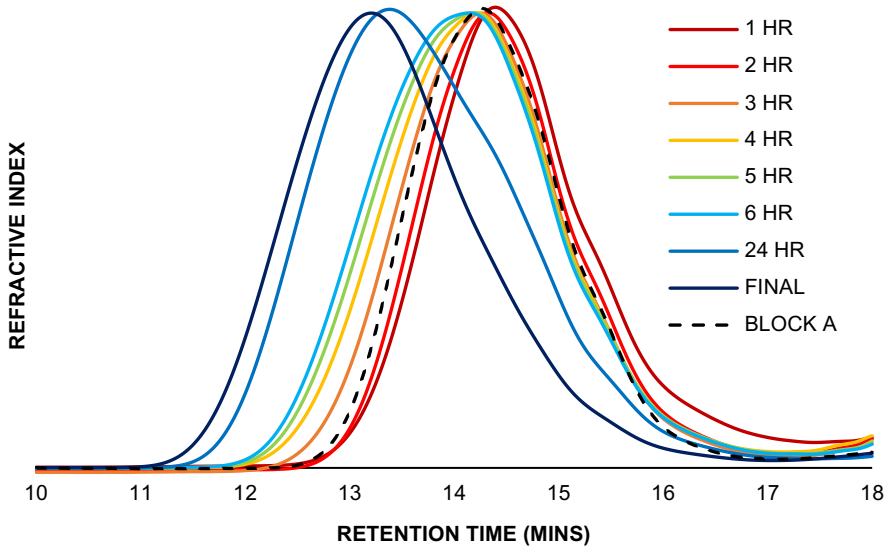


Figure 5.10. GPC traces for the kinetic samples taken for the preparation of PMMA-*b*-PS using 501 mg (0.05 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator with 522 mg (4.80 mmol) styrene. The reactions were conducted in 5 mL THF at 70 °C for 24 hours.

Figure 5.11 outlines FTIR the spectrum for the starting PMMA block and precipitated product. The stretching around 700 cm^{-1} is characteristic for the C-H bonding in monosubstituted benzene. The stretches resembling the functional groups of PMMA such as, a strong C=O carbonyl stretch at 1730 cm^{-1}, O-CH_3 stretch at 1250 cm^{-1}, and C-O bending at 1150 cm^{-1}. The results does not justify the production of a block copolymer.

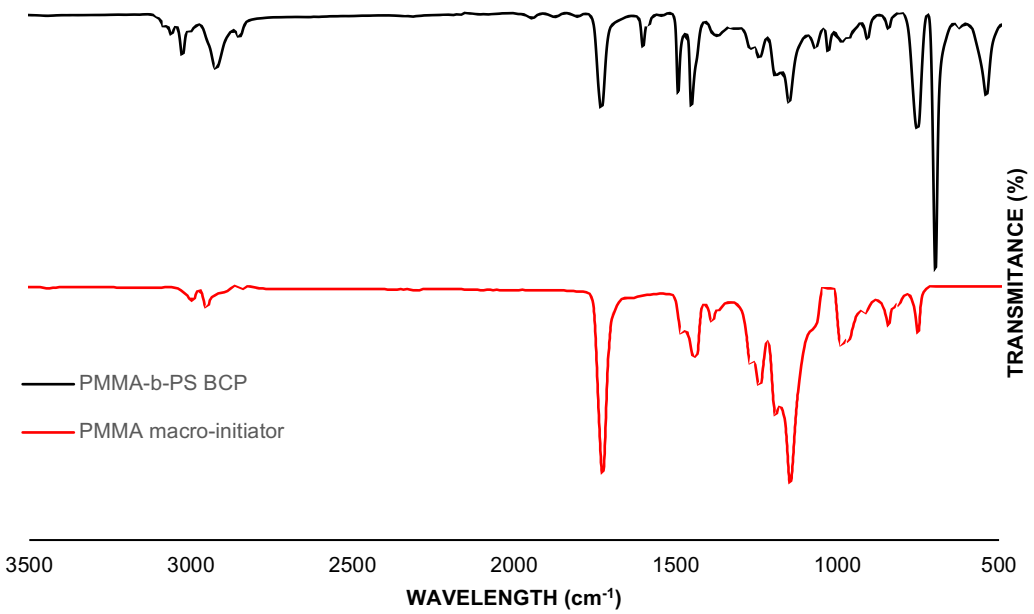


Figure 5.11. FTIR spectrum for PMMA used as the starting block and the precipitated polymer produced from the polymerisation of 522 mg (4.80 mmol) styrene using 501 mg (0.05 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

The DSC thermogram from the final heat cycle has been attached as Figure 5.12. The thermogram outlines two glass transition temperatures of equal intensity. A low temperature transition at 100 °C, is characteristic of PS and the high temperature transition at 130 °C is characteristic for PS. The intensity of each transition is very similar which suggest PMMA and PS are both in the final product with roughly equal mass.

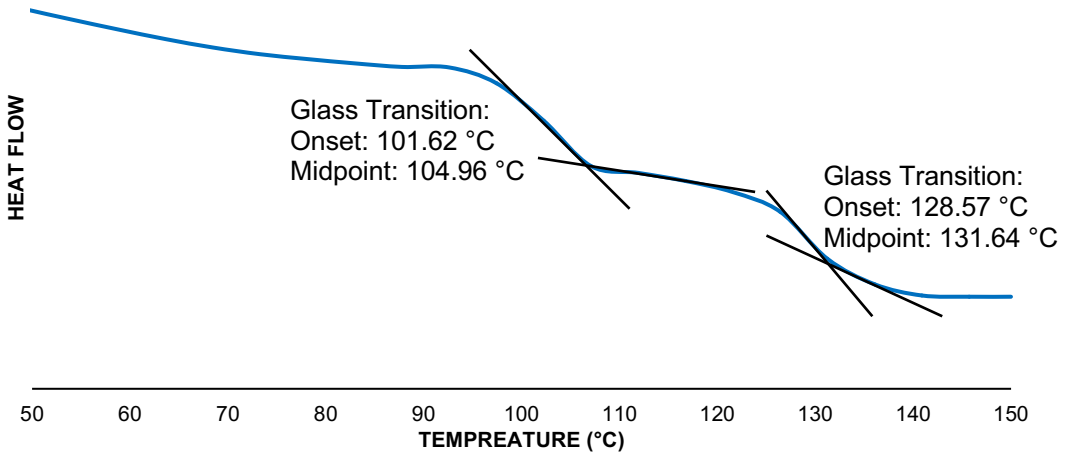


Figure 5.12. DSC thermogram for the polymer produced from the polymerisation of 522 mg (4.80 mmol) styrene using 501 mg (0.05 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

Thermogravimetric analysis (TGA) was used to investigate the thermal degradation of the copolymer. Figure 5.13 outlines the degradation curves for the precipitated block copolymer and the curves for PMMA and PS homopolymers. The degradation curve for the precipitated polymer shows a decomposition temperature of 305 °C. The polymer produced has better thermal stability compared to PMMA homopolymer which had a decomposition temperature of 289 °C but less thermally stable compared to PS homopolymer which had decomposition temperatures of 351 °C. This may suggest the polymer is amorphous and contains segments of both polymers.

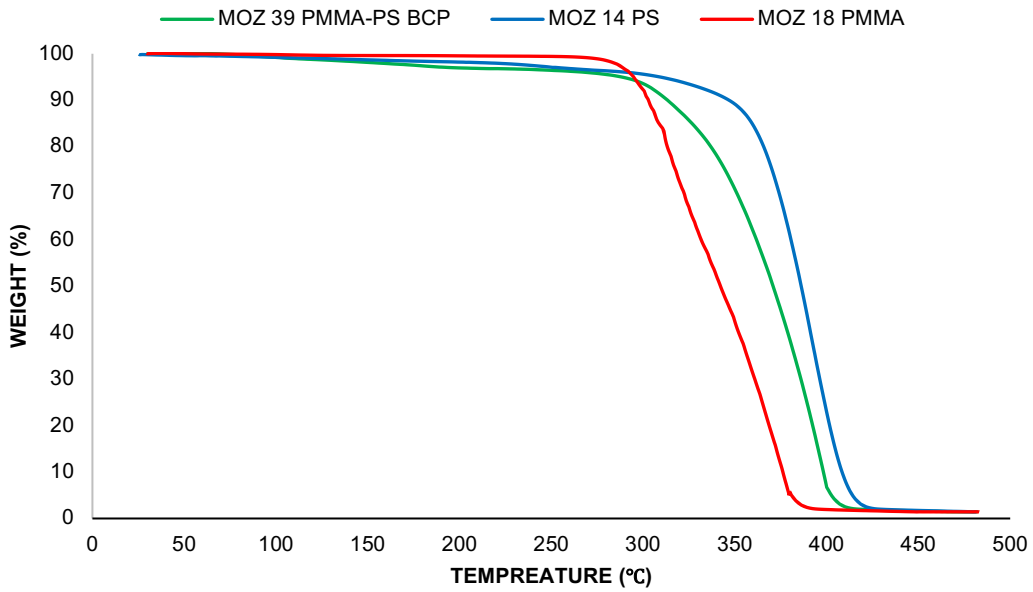


Figure 5.13. TGA degradation curve for the polymer produced from the polymerisation of 522 mg (4.80 mmol) styrene using 501 mg (0.05 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

DOSY experiments were performed to determine if the ^{1}H NMR signals belong to the same macromolecule. Figure 5.14 shows the DOSY spectra of the final polymer prepared in $CDCl_3$ (containing TMS as a reference), Figure 5.14 shows the ^{1}H signals corresponding to PMMA and PS are aligned on a different horizontal line indicating different diffusion coefficients. This indicates the presence of two species with different hydrodynamic radii instead of the desired block copolymer. The DOSY spectra suggests the peaks for the methyl and methylene group on PMMA had a different diffusion constant compared to the protons on the ester group and the protons on the PS chain. This suggest the ester group on PMMA diffused significantly quicker compared to the methylene and methyl group on the same chain. If the ^{1}H signals of both blocks had been perfectly aligned on the horizontal line of the DOSY, the pattern would have indicated that the signals belonged either to the same macromolecule or to molecules with the same diffusion coefficient. If so, the diffusion coefficient of the block copolymers PMMA-*b*-PS should be lower than that of the mixture of MMA and styrene homopolymers. Furthermore, when a given sample contains a mixture of block copolymers and homopolymer with different molecular weight, a deviation from pure mono exponential behaviour is observed.

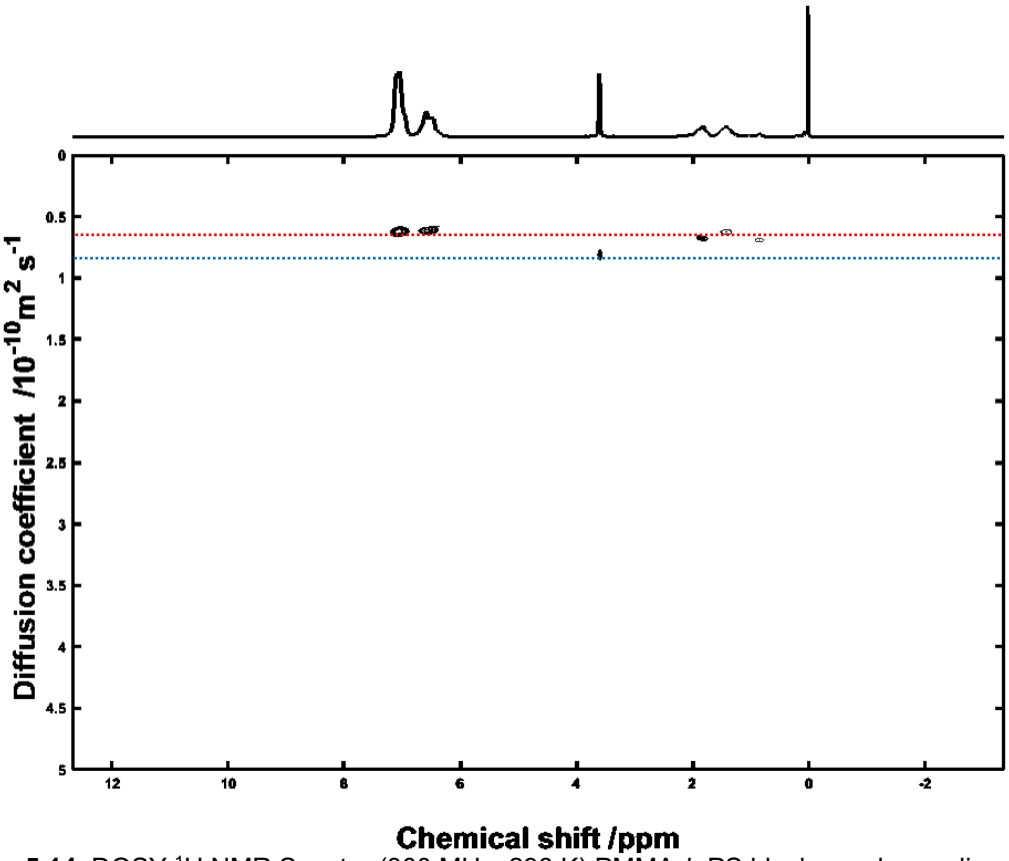


Figure 5.14. DOSY ^{1}H NMR Spectra (300 MHz, 298 K) PMMA-*b*-PS block copolymer dissolved in $CDCl_3$. The 1D spectra of the sample is shown above. The DOSY spectra shows two different species characterised by two different diffusion coefficients (0.62 x 10^{-10} m^2s^{-1} and 0.81 x 10^{-10} m^2s^{-1}) represented by the red and blue lines. The signals of PMMA have higher diffusion coefficient than the signals of PS. The rapidly diffusing $CDCl_3$ solvent peak is outside this region.

Table 5.4 shows the diffusion coefficient for the NMR signals from the precipitated polymer. The table shows a clear difference between the diffusion coefficient for the peaks resembling the ester group on PMMA and the signals for PS. The diffusion constant for the aromatic and methylene peaks which resemble PS have a diffusion coefficient of 0.62 x 10^{-10} m^2s^{-1}. The ester group for PMMA had a diffusion coefficient of 0.81 x 10^{-10} m^2s^{-1} whereas the methylene and methyl group of PMMA had a diffusion coefficient of 0.67 x 10^{-10} m^2s^{-1}. When taking into consideration the error in the diffusion coefficient the methylene group and methyl group from PMMA are very similar to the diffusion coefficient observed for PS block which could suggest the two blocks are connected.

Table 5.4. DOSY ^{1}H NMR (300 MHz) diffusion constants for the peaks present in the 1D spectra for the preparation of the PMMA-*b*-PS block copolymer. The block copolymer was prepared using 501 mg (0.05 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator with 522 mg (4.80 mmol) styrene. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

Chemical shift (ppm)	Diffusion constant (x 10^{-10} m^2s^{-1})	Error in diffusion constant (x 10^{-10} m^2s^{-1})	Allocation of peak
0.04	18.24	0.37	TMS in $CDCl_3$
1.02	0.67	0.24	(-CH_3) Methyl group on PMMA
1.45	0.63	0.24	(-CH_2-) Methylene chain on PS
1.85	0.67	0.24	(-CH_2-) Methylene chain on PMMA
3.64	0.81	0.24	(O-CH_3) Ester group on PMMA
6.61	0.62	0.23	(C-H) Proton on PS
7.08	0.62	0.23	(C-H) Aromatic Protons on PS

The PMMA starting material was examined using DOSY. The DOSY spectra for the PMMA starting material is shown in Figure 5.15. The spectra showa the diffusion coefficient of the ester group has a larger error compared to the methylene and methyl group on PMMA. The diffusion coefficient for the ester group was equal to 14.02 x 10^{-10} m^2s^{-1}. Figure 5.15 shows the diffusion coefficient for the homopolymer used is significantly larger compared to the coefficient of the PMMA protons in the block copolymer. This could suggests the formation of the block copolymer due to the coefficient of the ester protons on the new polymer being significantly lower compared to the starting material used. From further investigation, the ^{1}H NMR for each diffusion gradient resulted in distortion to some of the peaks. This was later discovered due to convection taking place in the tube due to the operating temperature of the machine.

Physical movements of the sample tube and/or pulsed field gradient coil can cause significant difficulties in diffusion measurements,[117] but one of the most troublesome sources if coherent sample motion is (Rayleigh Bernard) convection. When there is liquid at the top, there is a tendency for the warmer, and hence less dense, liquid to rise to the top, where it cools and then returns to the bottom in a continuous cycle. Convection only occurs when the temperature gradient exceeds a critical value, which depends in part on the sample geometry. In practice, convection in an NMR tube involves a (symmetric) spectrum of different flow rates which rapidly damps the cosine factor, but the qualitative conclusion remains that convection causes an accelerated decay of the signal. When

convection is slow, the effect on diffusion measurements is to increase the apparent diffusion coefficients; faster convection can lead to more complex flow patterns and to turbulence.[118]

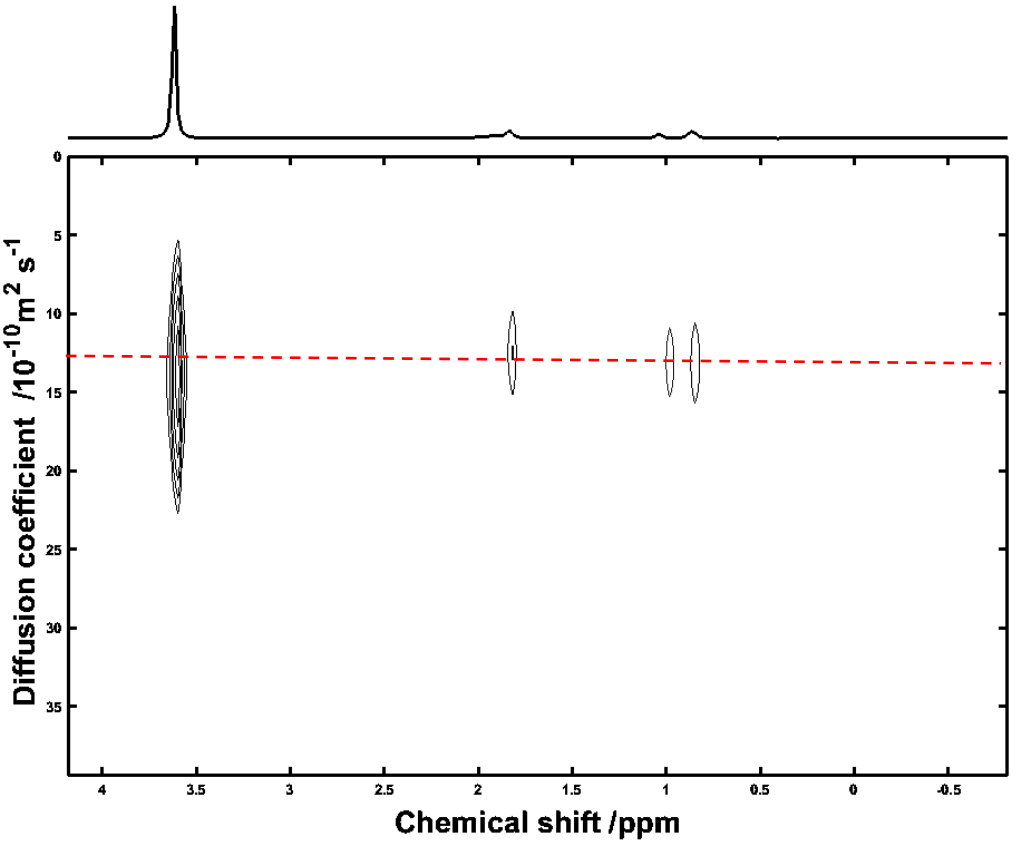


Figure 5.15. DOSY ^{1}H NMR spectra (300 MHz, 298 K) for the PMMA macroinitiator used in block copolymer synthesis dissolved in $CDCl_3$. The 1D spectra of the sample is shown above. The DOSY spectra shows one species characterised by a diffusion coefficient (14.02 x 10^{-10} m^2s^{-1}) outlined by a red line. The rapidly diffusing $CDCl_3$ solvent peak is outside this region.

To delay the onset of convection a number of modifications can be made. Firstly, a convention-compensated pulse sequences can be used. Secondly the sample radius can be reduced using a smaller diameter sample tube. Other options include reducing the sample height, by the use of restricted sample volume. Finally, a more viscous solvent can be used such as DMSO, as convection is less likely in viscous solutions.[119]

5.5. PREPARATION OF PMMA-*b*-PS USING PMMA AS A MACRO-INITIATOR WITH DIFFERENT TARGET DEGREES OF POLYMERISATION

Following the results from Section 5.2, the experiments were repeated but targeting polymers with different ratios. In this section we focus on the preparation of 1 g PMMA-*b*-PS in 5 mL THF. The target ratios of MMA to styrene units were the following; 10:90, 25:75, 40:60, 60:40, 75:25, and 90:10. For these experiments PMMA homopolymer (M_n = 24,000 g/mol, $Đ$ = 1.56) prepared from bromoform-mediated polymerisation using 0.2 molar equivalents AIBN with 1 molar equivalents bromoform as used as the macro-initiator**.**

5.5.1 Synthesis of PMMA-*b*-PS using PMMA as a macro-initiator with a target ratio of 10:90

The molar mass and monomer conversion data for the preparation of PMMA-*b*-PS with a target ratio of 10:90 is shown in Table 5.5. The reaction originally shows slow progression in monomer conversion for the first 6 hours. After 24 hours, 41 % conversion was achieved. The molar mass data shows an increase in observed molar mass for the sample taken during the first hour and the sample taken at 24 hours.. In general, the dispersity increases gradually for the duration of the polymerisation, which implies the formation of short chain homopolymers.

Table 5.5. Molar mass and monomer conversion data for the preparation of 1 g PMMA-*b*-PS with a target ratio of 10:90 using 102 mg (0.004 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator with 936 mg (9 mmol) styrene. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

Time (Hours)	Monomer Conversion (%) [(a)]	Observed M_n (g/mol) [(b)]	$Đ$ [(b)]
1	10	20,000	1.75
2	12	20,300	1.56
3	13	20,600	1.57
4	14	20,600	1.64
5	15	20,700	1.85
6	18	22,400	1.63
24	41	34,600	2.15
FINAL [(c)]	-	37,000	2.03

(a) Monomer conversion determined by ^{1}H NMR spectroscopy

(b) M_n and $Đ$ determined by GPC [polystyrene standards]

(c) Final polymer was isolated by precipitation in methanol

The ^{1}H NMR for the precipitated product in $CDCl_3$ is shown in Figure 5.16. The resonance signal at 3.55 ppm is attributed to the methyl ester group of PMMA. The signals in the region ranging from 1.65 to 1.95 ppm and from 0.65 and 1.02 ppm are attributed to the methylene and methyl group of atactic PMMA, respectively. The two resonance signals in the region of 7.56 ppm and 6.25 ppm are characteristic of benzyl protons and the resonance signals around 2.23 ppm represents methylene protons characteristic for PS. The spectra also contains signals for residual THF around 3.50 ppm and 1.75 ppm. The integrals of the polymer protons were used to calculate the actual ratio of each monomer unit present in the copolymer. The actual ratio was calculated to be 10:43.

Integrals of PMMA protons: Integrals of PS proton 3/3: 4.28/1 1: 4.28 10:43

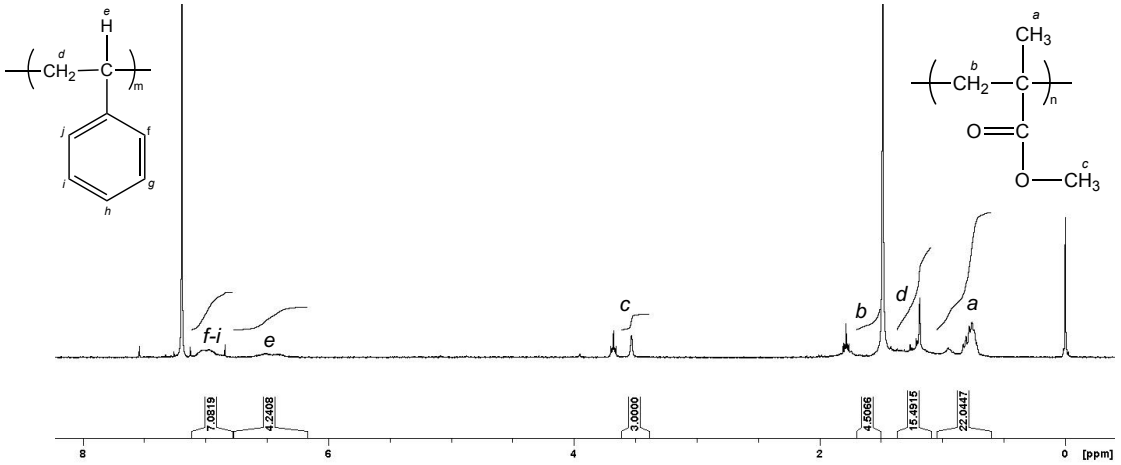


Figure 5.16. ^{1}H NMR spectra (300 MHz) for the precipitated polymer produced from the preparation of PMMA-*b*-PS with a target ratio of 10:90. The chemical structure of PMMA is shown st the top-right and PS in the top-left. The resonance labelled with low case letter are assigned to each particular chemical group.

Figure 5.17 outlines the GPC traces for the kinetic samples taken for the duration of the polymerisation. Initially the traces show no change in retention time for the first 4 hours. Following this period, a small difference is observed, suggesting an increase in chain length. Figure 5.17 shows the production of a shoulder on most traces, this is outlined clearly for the GPC trace at 24 hours. After the precipitation the shoulder peak for the final polymer disappears. Using the evidence from the NMR spectrum this is most likely PS homopolymer, which is removed after precipitation and filtration.

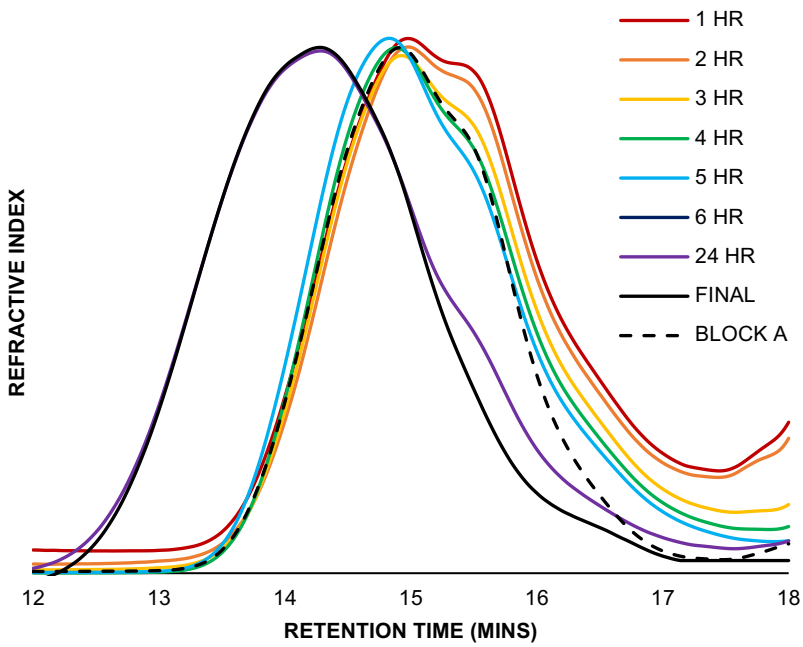


Figure 5.17. GPC traces for the kinetic samples taken for the preparation of PMMA-*b*-PS with a target ratio of 10:90 using 102 mg (0.004 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator with 936 mg (9 mmol) styrene. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

5.5.2 Synthesis of PMMA-*b*-PS using PMMA as a macro-initiator with a target ratio of 25:75

The molar mass and monomer conversion data for the preparation of PMMA-*b*-PS with a target ratio of 25:75 is shown in Table 5.6. The reaction initially shows slow progression in monomer conversion. The difference in observed molar mass was marginal for the first 6 hours, but after 24 hours a clear difference is observed when compared to the PMMA homopolymer used as the starting block. The molar mass data for the precipitated polymer had a lower dispersity compared to final kinetic sample, this suggest the removal of low molar mass polymer from the final product.

Table 5.6. Molar mass and monomer conversion data from the kinetic samples taken for the preparation of 1 g PMMA-*b*-PS with a target ratio of 25:75 using 251 mg (0.010 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator and 781 mg (7.51 mmol) styrene. The reaction was conducted in 5 mLTHF at 70 °C for 24 hours.

Time (Hours)	Monomer Conversion (%) [(a)]	Observed M_n (g/mol) [(b)]	$Đ$ [(b)]
1	6	19,400	1.66
2	9	19,500	1.78
3	10	20,400	1.69
4	12	20,500	1.67
5	14	20,600	1.80
6	17	20,800	1.78
24	50	31,600	2.46
FINAL [(c)]	-	36,000	2.30

(a) Monomer conversion determined by ^{1}H NMR spectroscopy

(b) M_n and $Đ$ determined by GPC [polystyrene standards]

(c) Final polymer was isolated by precipitation in methanol

The ^{1}H NMR for the precipitated polymer in $CDCl_3$ is outlined in Figure 5.18. The resonance signal at 3.55 ppm is attributed to the methyl ester group of PMMA. The signals in the region ranging from 1.65 to 1.95 ppm and from 0.65 and 1.02 ppm are attributed to the methylene and methyl group of atactic PMMA, respectively. The two resonance signals in the region of 7.56 ppm and 6.25 ppm are characteristic of benzyl protons and the resonance signals around 2.23 ppm represents methylene protons characteristic for PS. The spectra contain small signals around 3.60 ppm and 1.76 ppm which is characteristic for residual THF. The integrals of the polymer protons were used to calculate the actual ratio of each monomer unit present in the copolymer. The actual ratio was equal to 25:62.

Integrals of PMMA protons: Integral of PS proton 3/3: 2.48/1 1: 2.48 25:62

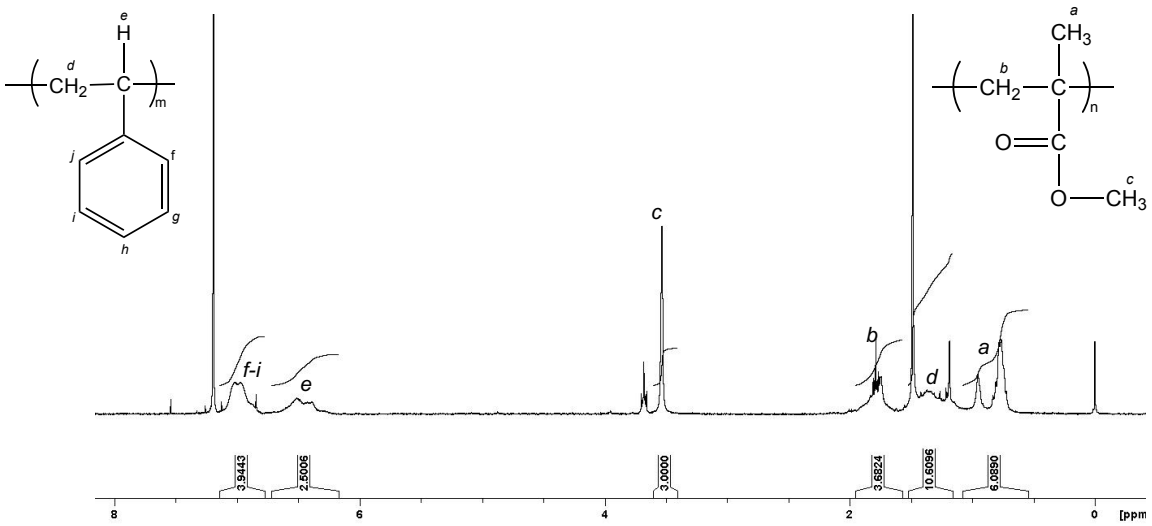


Figure 5.18. ^{1}H NMR spectra (300 MHz) for PMMA-*b*-PS with a target ratio of 25:75. Chemical structure of PMMA is shown in the top-right and PS in the top-left. The resonance labelled with low case letter are assigned to each particular chemical group.

Figure 5.19 outlines the GPC traces for the kinetic samples taken for the duration of the polymerisation. Initially the traces show no change in retention time for the first 6 hours. The GPC trace for the sample taken after 24 hours shows a clear difference in retention time. Figure 5.19 shows the production of a shoulder on most traces, this is clearly visible for the GPC trace taken at 24 hours. After precipitation, the intensity of the shoulder peak on the final polymer has decreased.

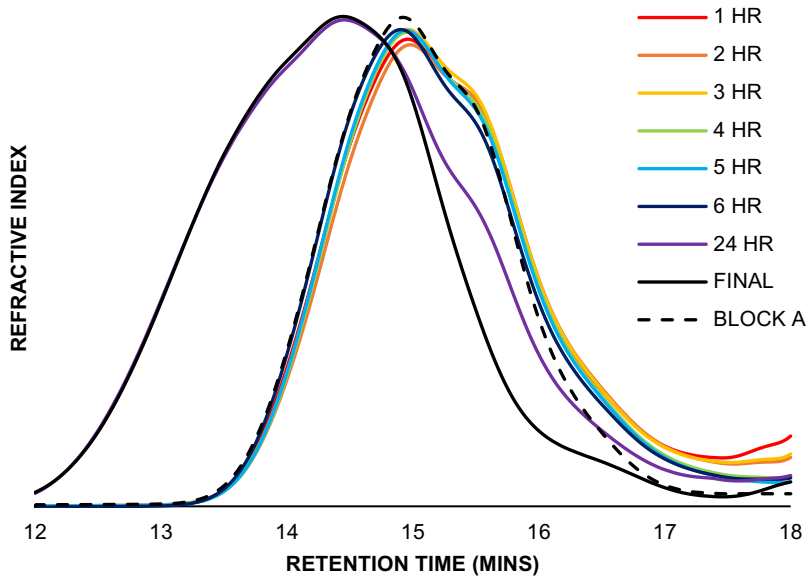


Figure 5.19. GPC traces for the kinetic samples taken for the preparation of PMMA-*b*-PS with a ratio of 25:75 using 251 mg (0.01 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator and 781 mg (7.51 mmol) styrene. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

5.5.3 Synthesis of PMMA-*b*-PS using PMMA as a macro-initiator with a target ratio of 40:60

The molar mass and monomer conversion data for the preparation of PMMA-*b*-PS with a target ratio of 40:60 is shown in Table 5.7. The reaction originally shows fast progression in monomer conversion. The molar mass data suggests a marginal difference for the first 6 hours. After 24 hours a clear difference is observed between the starting material and the molar mass for the polymers at this interval. The change in molar mass, implies the length of the final polymer has increased. In general, the dispersity increases for the duration of the polymerisation, which suggests the formation of PS homopolymer.

Table 5.7. Molar mass and monomer conversion data from the kinetic samples taken for the preparation PMMA-*b*-PS with a target ratio of 40:60 using 404 mg (0.017 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator and 621 mg (5.97 mmol) styrene. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

Time (Hours)	Monomer Conversion (%) [(a)]	Observed M_n (g/mol) [(b)]	$Đ$ [(b)]
1	27	20,700	1.65
2	29	18,300	1.96
3	37	19,100	1.77
4	39	19,000	1.79
5	43	19,300	1.77
6	59	19,100	1.94
24	97	27,900	2.00
FINAL [(c)]	-	31,000	2.87

(a) Monomer conversion determined by ^{1}H NMR spectroscopy

(b) M_n and $Đ$ determined by GPC [polystyrene standards]

(c) Final polymer was isolated by precipitation in methanol

The ^{1}H NMR for the precipitated polymer in $CDCl_3$ is shown in Figure 5.20. The resonance signal at 3.55 ppm is attributed to the methyl ester group of PMMA. The signals in the region ranging from 1.65 to 1.95 ppm and from 0.65 and 1.02 ppm are attributed to the methylene and methyl group of atactic PMMA, respectively. The two resonance signals in the region of 7.56 ppm and 6.25 ppm are characteristic of benzyl protons and the resonance signals around 2.23 ppm represents methylene protons characteristic for PS.The integrals of the polymer protons were used to calculate the actual ratio of each monomer unit present in the copolymer. The actual ratio was 40:57.

Integrals of PMMA protons: Integral of PS proton 3/3: 1.43/1 1: 1.43 40:57

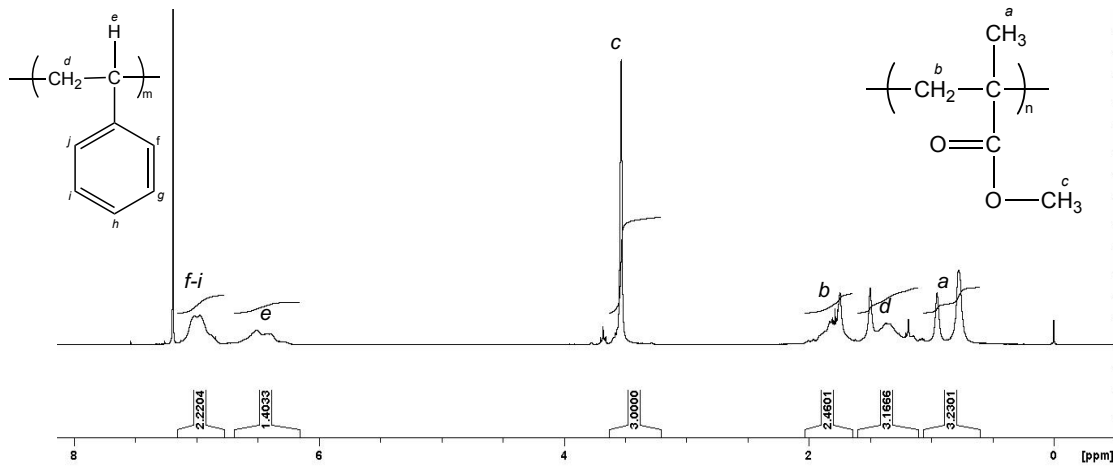


Figure 5.20. ^{1}H NMR spectra (300 MHz) for PMMA-*b*-PS with a target ratio of 40:60. The chemical structure of PMMA is shown in the top-right and PS in the top-left. The resonance labelled with low case letter are assigned to each particular chemical group.

The ^{1}H NMR suggests the formation of PS during the polymerisation. Figure 5.21 shows the GPC traces for the kinetic samples taken for the polymerisation. The traces show no change in retention time for the samples taken in the first 6 hours. The sample taken at 24 hours shows a small difference in retention time, suggesting an increase in chain length. Figure 5.21 shows the appearance of a shoulder for most traces around 16.5 mins, which could be from the formation of low molar mass PS. After precipitation, the shoulder for the final polymer is observed at longer retention time. This suggests the formation of 'high' molar mass polymers or a mixture of products. The information from ^{1}H NMR, suggests the formation of the block copolymer or high molar mass PS.

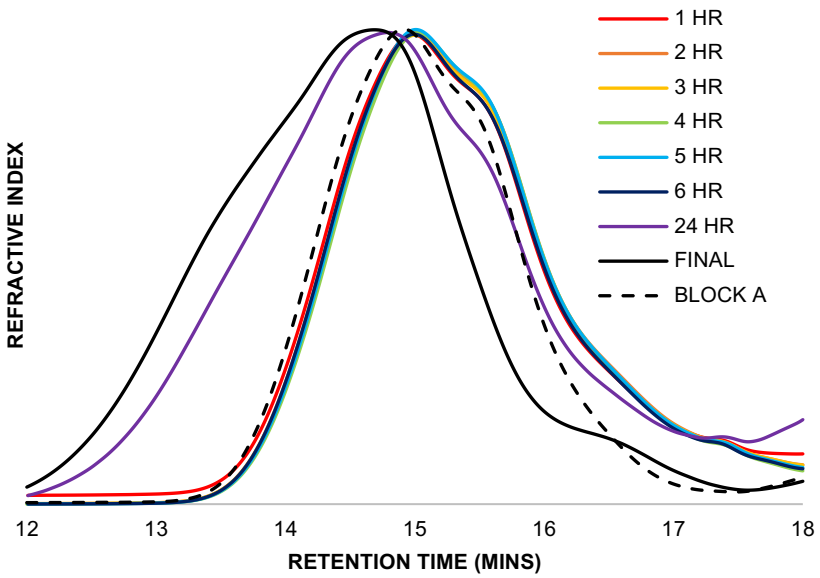


Figure 5.21. GPC traces for the kinetic samples taken for the preparation of PMMA-*b*-PS with a target ratio of 40:60 using 404 mg (0.017 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator and 621 mg (5.97 mmol) styrene. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

5.5.4 Synthesis of PMMA-*b*-PS using PMMA as a macro-initiator with a target ratio of 60:40

The molar mass and monomer conversion data for the preparation of PMMA-*b*-PS with a target ratio of 60:40 is shown in Table 5.8. The molar mass data show a marginal difference between M_n for the starting materials and the samples taken for the first 6 hours. After 24 hours a small difference is observed between the molar masses. In general, the dispersity increases gradually for the duration of the polymerisation, which implies the formation of PS homopolymer.

Table 5.8. Molar mass and monomer conversion data from the kinetic samples taken for the preparation of 1 g PMMA-*b*-PS with a target ratio of 60:40, using 603 mg (0.025 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator and 410 mg (3.94 mmol) styrene. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

Time (Hours)	Monomer Conversion (%) [(a)]	Observed M_n (g/mol) [(b)]	$Đ$ [(b)]
1	54	20,500	1.72
2	57	20,100	1.71
3	60	19,700	1.89
4	62	18,000	2.05
5	64	20,200	1.61
6	68	18,700	2.19
24	92	21,700	2.53
FINAL [(c)]	-	26,000	2.68

(a) Monomer conversion determined by ^{1}H NMR spectroscopy

(b) M_n and $Đ$ determined by GPC [polystyrene standards]

(c) Final polymer was isolated by precipitation in methanol

The ^{1}H NMR for the precipitated polymer in $CDCl_3$ is shown in Figure 5.22. The resonance signal at 3.55 ppm is attributed to the methyl ester group of PMMA. The signals in the region ranging from 1.65 to 1.95 ppm and from 0.65 and 1.02 ppm are attributed to the methylene and methyl group of atactic PMMA, respectively. The two resonance signals in the region of 7.56 ppm and 6.25 ppm are characteristic of benzyl protons and the resonance signals around 2.23 ppm represents methylene protons characteristic for PS.The integrals of the polymer protons were used to calculate the actual ratio of each monomer unit present in the copolymer. The actual ratio was calculated to be 60:57.

Integrals of PMMA protons: Integral of PS proton 3/3: 0.95/1 1: 0.95 60:57

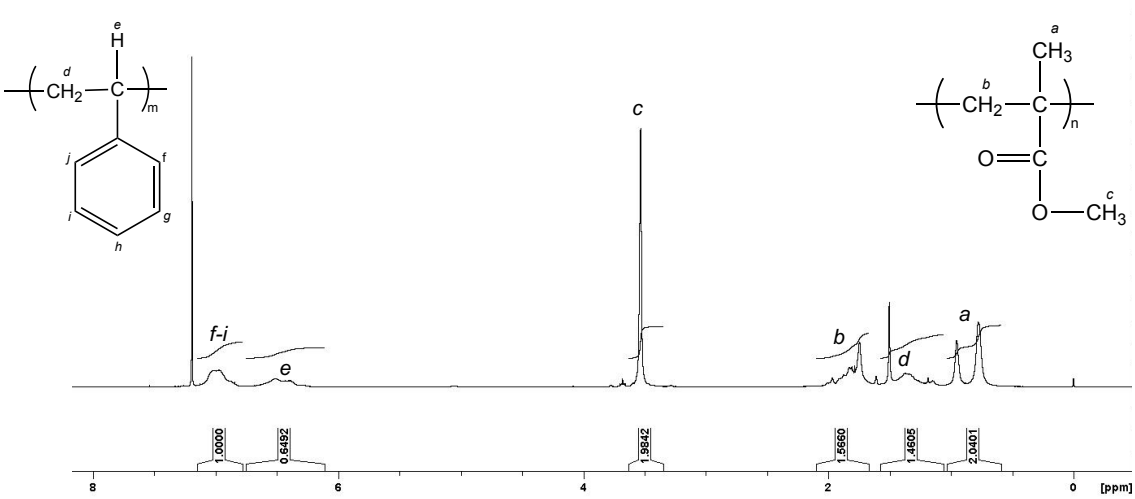


Figure 5.22. ^{1}H NMR spectra (300 MHz) for PMMA-*b*-PS with a target ratio of 60:40. Chemical structure of PMMA is shown in the top-right and PS in the top-left. The resonance labelled with low case letter are assigned to each particular chemical group.

Figure 5.23 shows the GPC traces for the kinetic samples taken for the polymerisation. The traces show no change in retention time for the samples taken in the first 6 hours. The trace for the sample taken at 24 hours shows a small difference in retention time. Figure 5.23 shows the production of a shoulder for majority traces. After precipitation, a small lump is visible on the trace for the final polymer. The information from ^{1}H NMR suggests the production of low molar mass PS homopolymer or an impurity.

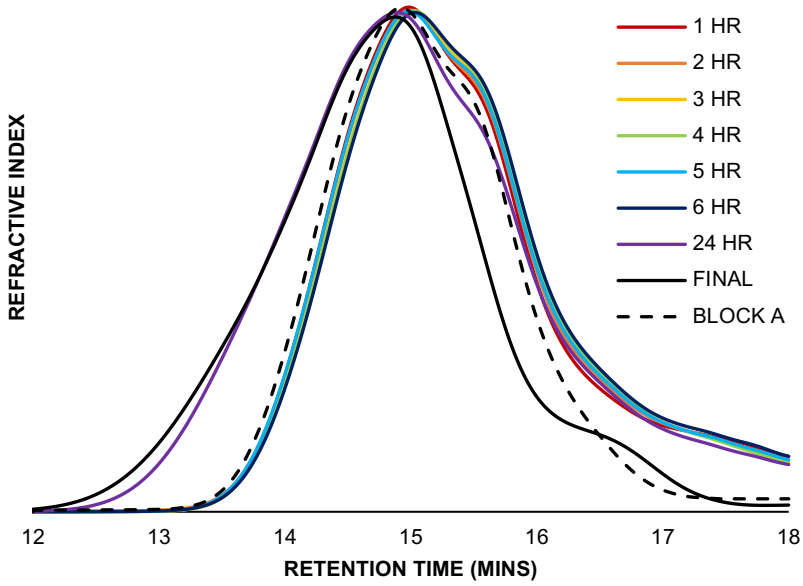


Figure 5.23. GPC traces for the kinetic samples taken for the preparation of PMMA-*b*-PS with a target ratio of 60:40 using 603 mg (0.025 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator and 410 mg (3.94 mmol) styrene. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

5.5.5 Synthesis of PMMA-*b*-PS using PMMA as a macro-initiator with a target ratio of 75:25

The molar mass and monomer conversion data for the preparation of PMMA-*b*-PS with a target ratio of 75:25 is shown in Table 5.9. The reaction originally shows a slow progression in monomer conversion. After 6 hours the conversion was equal to 7 % and after 24 hours, 64 % was achieved. The molar mass data shows a small difference for the change in molar mass for the samples taken for the first 6 hours.

Table 5.9. Molar mass and monomer conversion data from the kinetic samples taken for the preparation of 1 g PMMA-*b*-PS with a target ratio of 75:25 using 750 mg (0.031 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator and 259 mg (2.49 mmol) styrene. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

Time (Hours)	Monomer Conversion (%) [(a)]	Observed M_n (g/mol) [(b)]	$Đ$ [(b)]
1	0	20,400	1.77
2	0	20,700	1.72
3	0	20,500	1.72
4	0	21,000	1.79
5	5	21,600	1.81
6	7	21,900	1.73
24	64	22,900	1.87
FINAL [(c)]	-	26,000	2.03

(a) Monomer conversion determined by ^{1}H NMR spectroscopy

(b) M_n and $Đ$ determined by GPC [polystyrene standards]

(c) Final polymer was isolated by precipitation in methanol

The ^{1}H NMR for the precipitated product in $CDCl_3$ is presented in Figure 5.24. The resonance signal at 3.55 ppm is attributed to the methyl ester group of PMMA. The signals in the region ranging from 1.65 to 1.95 ppm and from 0.65 and 1.02 ppm are attributed to the methylene and methyl group of atactic PMMA, respectively. The two resonance signals in the region of 7.56 ppm and 6.25 ppm are characteristic of benzyl protons and the resonance signals around 2.23 ppm represents methylene protons characteristic for PS.The integrals of the polymer protons were used to calculate the actual ratio of each monomer unit present in the copolymer. The actual ratio was equal to 75:17.

Integrals of PMMA Protons: Integral of PS Proton 3/3: 0.23/1 1: 0.23 75:17

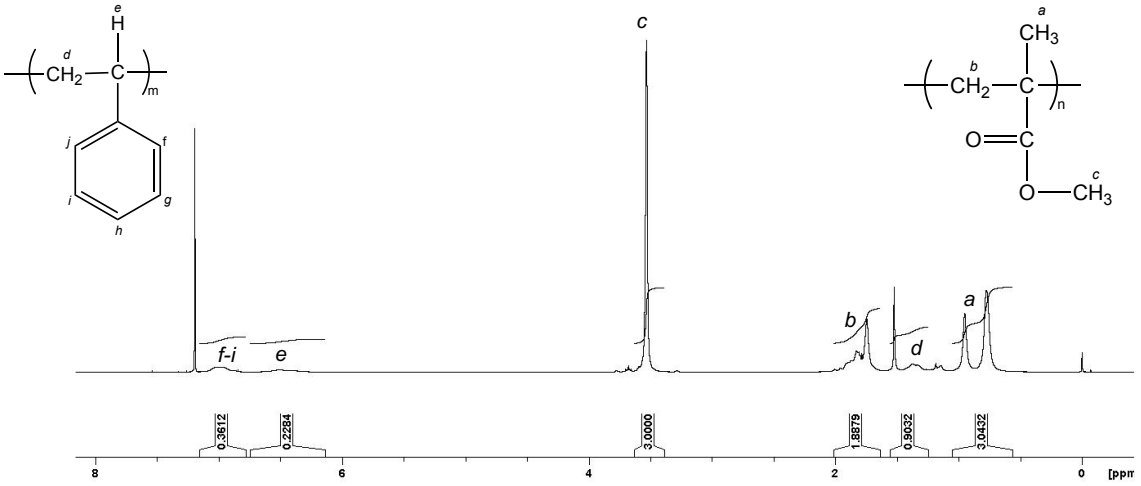


Figure 5.24. ^{1}H NMR spectra (300 MHz) for PMMA-*b*-PS with a target ratio of 75:25. The Chemical structure of PMMA is shown at the top-right and PS at the top-left. The resonance labelled with low case letter are assigned to each particular chemical group.

Figure 5.25 outlines the GPC traces for the kinetic samples taken for the polymerisation. The traces show no significant change in retention time for all kinetic samples taken. Figure 5.25 shows the production of a shoulder peak for majority of the kinetic samples taken. After precipitation, the shoulder on most GPC traces is removed. This suggests the low molar mass polymer has been removed. The trace for the final polymer shows the presence of 'high' molar mass polymers being formed, which could be 'high' molar mass PS or block copolymer.

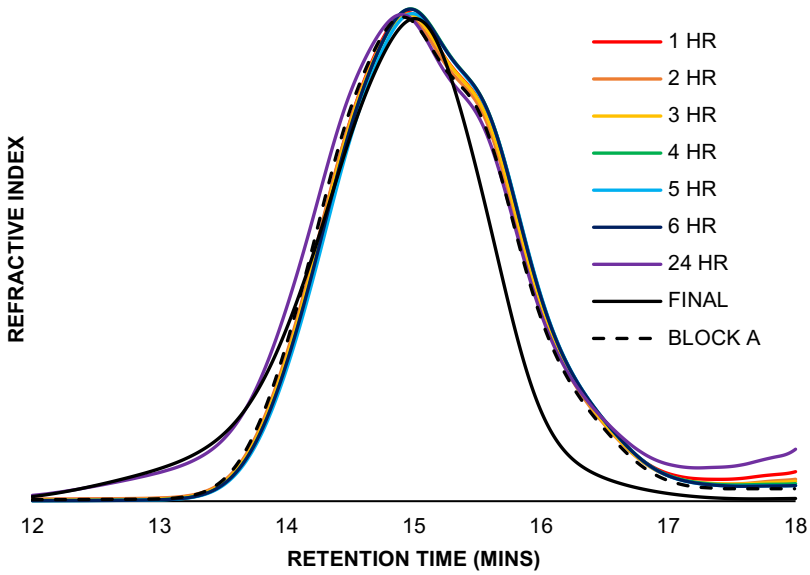


Figure 5.25. GPC traces for the kinetic samples taken for the preparation of PMMA-*b*-PS with a target ratio of 75:25 using 750 mg (0.031 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator and 259 mg (2.49 mmol) styrene. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

5.5.6 Synthesis of PMMA-*b*-PS using PMMA as a macro-initiator with a target ratio of 90:10

The molar mass and monomer conversion data for the preparation of PMMA-*b*-PS with a target ratio of 90:10 is shown in Table 5.10. The reaction shows slow progression in monomer conversion. The molar mass data shows a marginal difference between each sample taken for the duration of the polymerisation observed molar mass for the duration of the reaction. The results for the precipitated polymers show a significant difference between the observed molar mass and dispersity.

Table 5.10. Molar mass and monomer conversion data from the kinetic samples taken for the preparation of 1 g PMMA-*b*-PS with a target ratio of 75:25 using 901 mg (0.038 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator and 105 mg (1.00 mmol) styrene. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

Time (Hours)	Monomer Conversion (%) [(a)]	Observed M_n (g/mol) [(b)]	$Đ$ [(b)]
1	0	20,500	1.65
2	0	20,500	1.74
3	0	20,600	1.74
4	0	20,600	1.71
5	0	20,800	1.70
6	9	21,400	1.70
24	32	22,600	1.62
FINAL [(c)]	-	26,000	1.45

(a) Monomer conversion determined by ^{1}H NMR spectroscopy

(b) M_n and $Đ$ determined by GPC [polystyrene standards]

(c) Final polymer was isolated by precipitation in methanol

The ^{1}H NMR for the precipitated polymer in $CDCl_3$ is shown in Figure 5.26. The resonance signal at 3.55 ppm is attributed to the methyl ester group of PMMA. The signals in the region ranging from 1.65 to 1.95 ppm and from 0.65 and 1.02 ppm are attributed to the methylene and methyl group of atactic PMMA, respectively. The two resonance signals in the region of 7.56 ppm and 6.25 ppm are characteristic of benzyl protons and the resonance signals around 2.23 ppm represents methylene protons characteristic for PS. The integrals of the polymer protons were used to calculate the actual ratio of each monomer unit present in the copolymer. The actual ratio was equal to 90:2.

Integrals of PMMA Protons: Integral of PS Proton 3/3: 0.02/1 1: 0.02 90:2

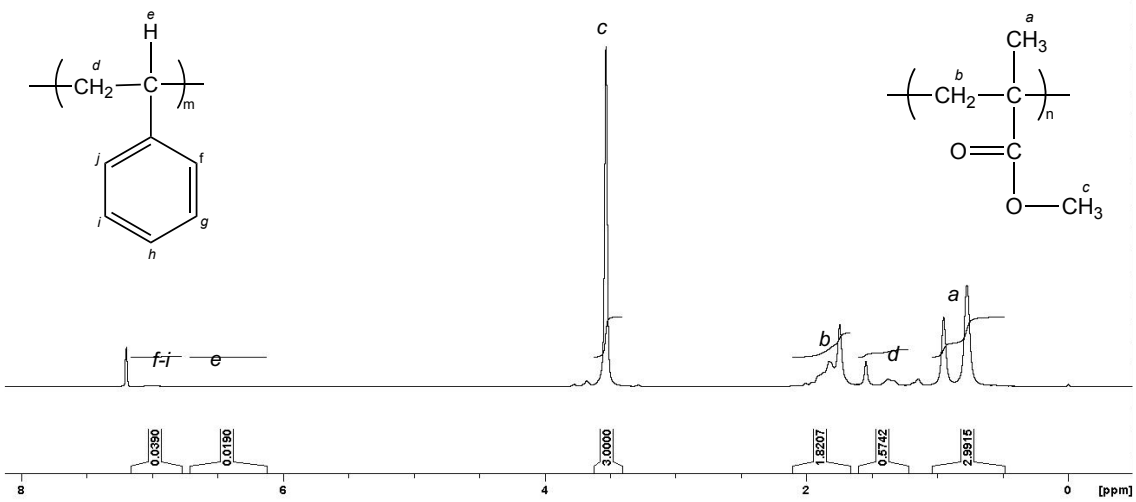


Figure 5.26. ^{1}H NMR spectra (300 MHz) for PMMA-*b*-PS with a target ratio of 90:10. Chemical structure of PMMA is shown at the top-right and PS at the top-left. The resonance labelled with low case letter are assigned to each particular chemical group.

Figure 5.27 outlines the GPC traces for the kinetic samples taken for the polymerisation. The traces show no change in retention time for all kinetic samples. Figure 5.27 shows the production of a shoulder for majority of the traces, which is most likely from PS homopolymer. After precipitation, the shoulder observed at longer retention time is no longer visible, which suggests the low molar mass homopolymer has been removed.

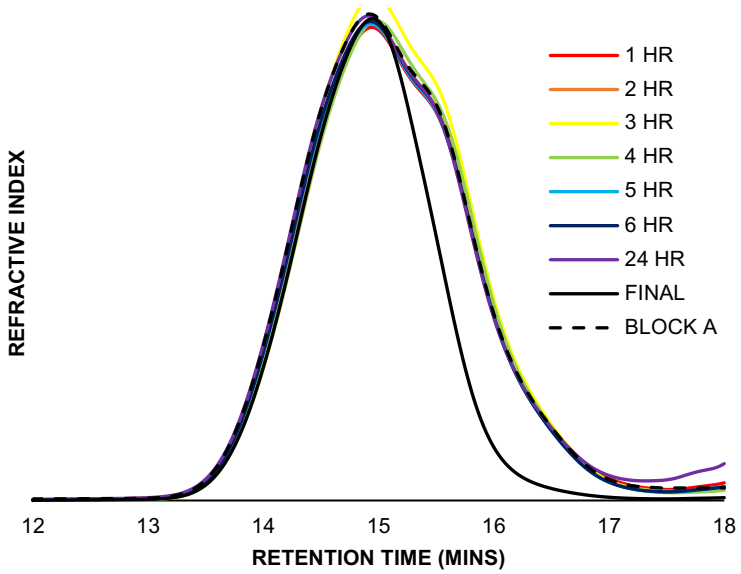


Figure 5.27. GPC traces for the kinetic samples taken for the preparation of PMMA-*b*-PS with a target ratio of 90:10 using 901 mg (0.038 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator and 105 mg (1.00 mmol) styrene. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

A summary of the results obtained from the block copolymer studies with different target degree of polymerisation is shown in Section 5.7.

5.6. SYNTHESIS OF PMMA-*b*-PS USING PMMA AS A MACRO-CTA

For this section PMMA homopolymer prepared from the thermal polymerisation of MMA using 0.2 molar equivalents AIBN with 1 molar equivalents bromoform was used as a macro-CTA. The progression of molar mass and monomer conversion for this experiment is shown in Table 5.11. The molar mass data for the precipitated polymer shows a significant decrease in molar mass and an increase in dispersity.

Table 5.11. Molar mass data for the preparation of PMMA-*b*-PS using 502 mg (0.05 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-CTA, 520 mg (4.80 mmol) styrene and 0.2 molar equivalents AIBN in 5 mL THF at 70 °C for 24 hours.

Time (Hours)	Monomer Conversion (%) [(a)]	Observed M_n (g/mol) [(b)]	$Đ$ [(b)]
1	29	22,000	1.62
2	34	23,000	1.63
3	36	23,000	1.60
4	39	18,000	1.80
5	40	16,000	1.93
6	42	14,000	2.20
24	98	13,000	1.84
FINAL [(c)]	-	5,000	4.52

(a) Monomer conversion determined by ^{1}H NMR spectroscopy

(b) M_n and $Đ$ determined by GPC [polystyrene standards]

(c) Final polymer was isolated by precipitation in methanol

The ^{1}H NMR for the precipitated product in $CDCl_3$ is shown in Figure 5.28. The resonance signal at 3.55 ppm is attributed to the methyl ester group of PMMA. The signals in the region ranging from 1.65 to 1.95 ppm and from 0.65 and 1.02 ppm are attributed to the methylene and methyl group of atactic PMMA, respectively. The two resonance signals in the region of 7.56 ppm and 6.25 ppm are characteristic of benzyl protons and the resonance signals around 2.23 ppm represents methylene protons characteristic for PS.The integrals of the polymer protons were used to calculate the actual ratio of each monomer unit present in the copolymer. The actual ratio was calculated to be 50:60.

Integrals of PMMA Protons: Integral of PS Proton 3/3: 1.20/1 1: 1.20 50:60

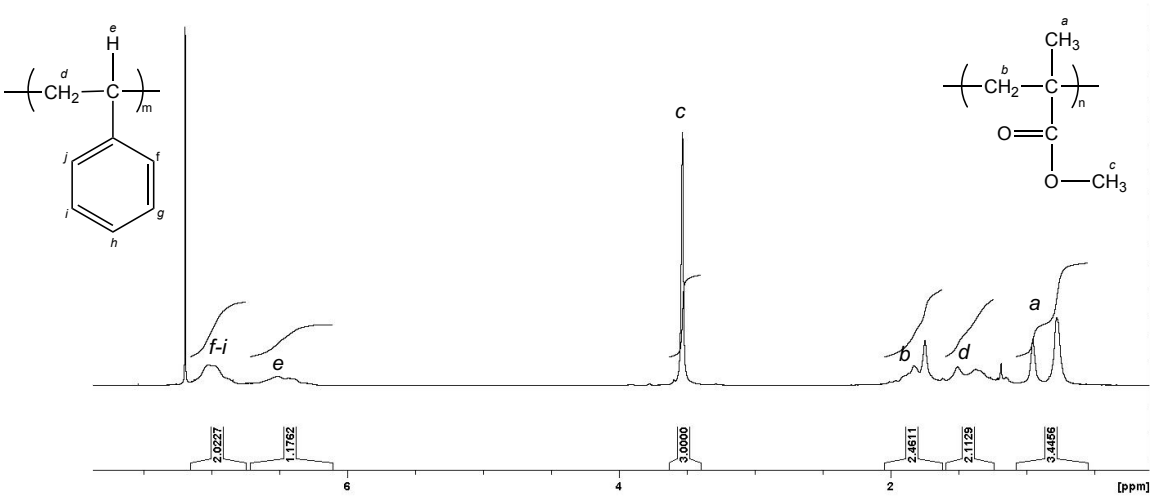


Figure 5.28. ^{1}H NMR spectra (300 MHz) for the preparation of PMMA-*b*-PS block copolymer. Chemical structure of PMMA is shown at the top-right and PS at the top-left. The resonance labelled with low case letter are assigned to each particular chemical group.

Figure 5.29 outlines the GPC traces for the kinetic samples taken for the duration of the polymerisation. The GPC trace shows no change in retention time for each sample taken. This suggests the second monomer unit has not successfully added onto the PMMA chain. Figure 5.29 shows the presence of a shoulder on each trace, this increases as the reaction progresses. Using the information from ^{1}H NMR, the shoulder is from PS homopolymer. This suggests the addition of AIBN has resulted in the radical polymerisation of styrene.

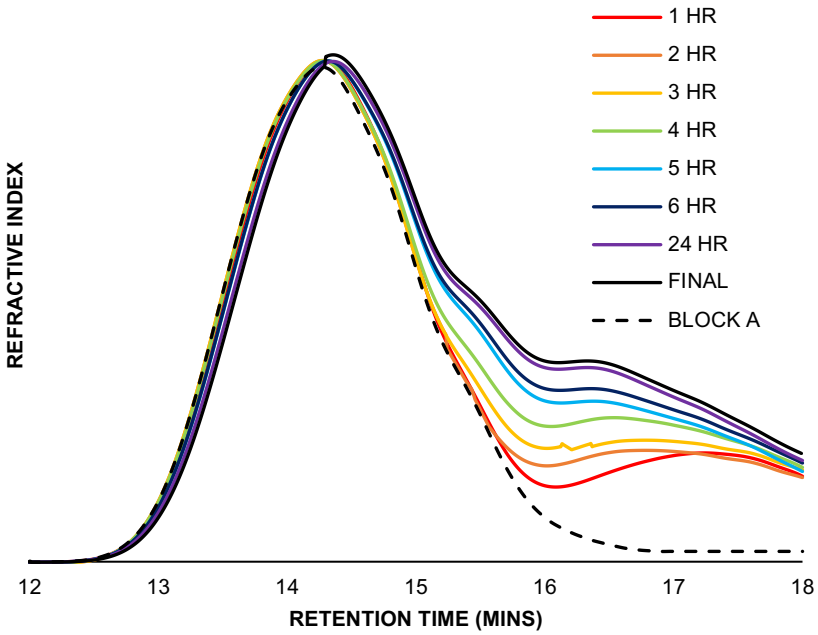


Figure 5.29. GPC traces for the kinetic samples taken for the preparation of PMMA-*b*-PS using 501 mg (0.05 mmol) PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-CTA with 522 mg (4.80 mmol) styrene and 0.2 molar equivalents AIBN. The reaction was conducted in 5 mL at 70 °C for 24 hours.

Figure 5.30 outlines the FTIR spectrum for the precipitated polymer. The stretching around 700 cm^{-1} is characteristic for the C-H bonding in monosubstituted benzene. The spectrum contained stretches resembling the functional groups of PMMA such as, a strong C=O carbonyl stretch at 1730 cm^{-1}, O-CH_3 stretch at 1250 cm^{-1}, and C-O bending at 1150 cm^{-1}. The results does not justify the production of a block copolymer.

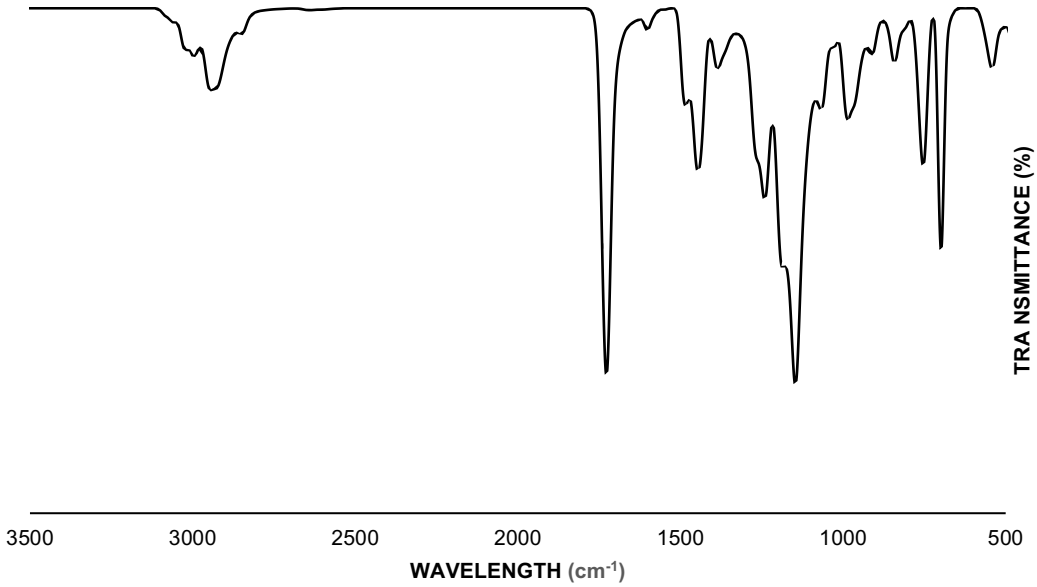


Figure 5.30. FTIR spectrum for the precipitated polymer produced from the polymerisation of 522 mg (4.80 mmol) styrene using 501 mg (0.05 mmol) PMMA as a macro-CTA and 0.2 molar equivalents AIBN. The reaction was conducted in 5 mL THF at 70 °C for 24 hours.

5.7. CONCLUSIONS

For the preparation of PMMA-PS copolymer, the selection of the homopolymer used as a macroinitiator plays an important role. The results show the monomer with the slower propagating rate coefficient should be used as the monomer which adds on to starting macro-monomer. This is surprising as the activation energy for the propagation of MMA monomer (E_a (30 °C) = 20.2 kJ mol^{-1}) is smaller compared to styrene (E_a (30 °C) = 32.5 kJ mol^{-1}).[109] A summary of the molar mass data obtained from the GPC traces and the conversion achieved after 24 hours for the preparation of different ratio PMMA-*b*-PS using PMMA is shown in Table 5.12. The results show the molar mass of the polymer increase when a larger quantity of styrene is used compared to the PMMA macro-initiator. A significant increase in molar mass is observed when the target ratio was 50:50. This implied a larger number of styrene units had successfully added onto the PMMA chain, or PS homopolymer is present in the final polymer. Majority of the copolymers produced with different degree of polymerisation had observed ratios very close to the target ratio. Due to kinetic studies being conducted on these experiments, the observed molar mass of the final polymer could be significantly different.

Table 5.12. Molar mass and monomer conversion data for the preparation 1 g PMMA-*b*-PS with target ratios of 10:90, 25:75, 40:60, 60:40, 75:25, and 90:10 using PMMA (M_n = 24,000 g/mol, $Đ$ = 1.56) as a macro-initiator. The reactions were conducted in 5 mL THF at 70 °C for 24 hours and the final polymers were isolated by precipitation in methanol.

Code	Target ratio of MMA:St (a)	Actual ratio of MMA:St (b)	Monomer conversion (%) (c)	Observed M_n (g/mol) (d)	$Đ$ (d)	*Success* (e)
MOZ 39A	10:90	10:43	41	37,000	2.03	Yes
MOZ 39B	25:75	25:62	50	36,000	2.30	Yes
MOZ 39C	40:60	40:57	97	31,000	2.87	Yes
MOZ 39	50:50	50:170	98	54,000	2.41	Yes
MOZ 39D	60:40	60:57	98	26,000	2.68	Yes
MOZ 39E	75:25	75:17	64	26,000	2.03	No
MOZ 39F	90:10	90:2	32	26,000	1.45	No

(a) Target ratio of MMA and styrene units in copolymer, determined by GPC [poly(methyl methacrylate) standards]

(b) Actual ratio of MMA to styrene units in final polymer, determined by ^{1}H NMR spectroscopy of the precipitated polymer.

(c) Monomer conversion after 24 hours determined by ^{1}H NMR spectroscopy

(d) M_n and $Đ$ determined by GPC [polystyrene standards]

(e) Reaction is based as a success from evidence from GPC traces and ^{1}H NMR spectroscopy

(f) Experiments were conducted once, due to limited time constraints

Figure 5.31 outlines the overlaid GPC traces for each of the precipitated polymer with different target ratios. The traces show the largest difference in retention time is observed for the polymers produced with a target ratio of 50:50 between MMA units and styrene units. The other traces show a shorter retention time (larger M_n) is observed for the polymers produced when a large concentration of styrene is added to a small amount of PMMA. This cound suggests having a large quantity of styrene units in the reaction flask, increases its likelihood of finding the active centre to start chain propagation. The results from the polymer produced with a target ratio 50:50 does not follow this pattern. To ensure the conclusion is reliable and accurate, the experiments should be repeated with and without taking kinetic samples.

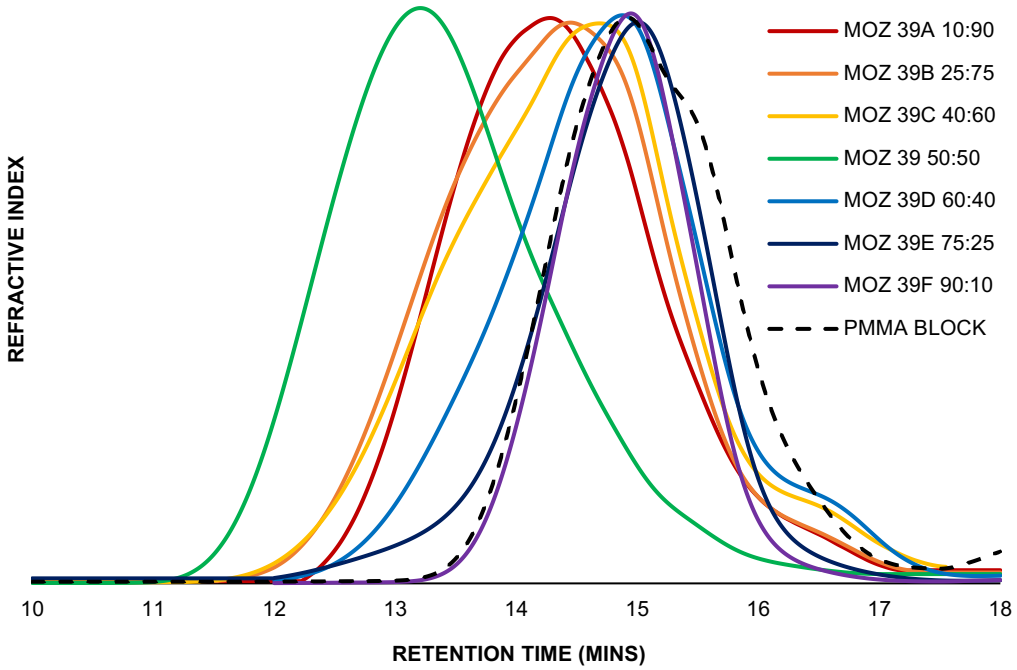


Figure 5.31. GPC traces for the precipitated polymers produced from using PMMA as a macro-initiator for the polymerisation of styrene monomer. The reactions were conducted in 5 mLTHF at 70 °C for 24 hours. The polymers produced had target ratios of; 10:90, 25:75, 40////.|60, 50:50, 60:40, 75:25, and 90:10.

From the current analytical techniques available, it was difficult to identify the structure of the copolymer formed. The only effective techniques were DOSY ^{1}H NMR and GPC. DOSY ^{1}H NMR was useful when identifying if a block copolymer had been formed or a collection of PMMA and PS homopolymer was formed. Due to limited time constraints and equipment availability, DOSY experiments were not conducted on all polymer samples. The molar ratio of styrene monomer to PMMA macro-initiators could be used, to try produce polymers with closer target degree of polymerisation.

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1. CONCLUSIONS

The applications of block copolymers have been used in a wide range of industries. In medicinal research, the production of amphiphilic block copolymers has gained a lot of interest, especially temperature and pH-responsive copolymers. The current methods used for the block copolymer synthesis include anionic, cationic polymerisations and mainly controlled radical polymerisation techniques such as RAFT, ATRP and NMP. The CRP methods have many drawbacks such as a limited selection of monomers for ATRP, specific reaction conditions required for NMP and expensive purchasing price for RAFT agents.

Alternatives to these well-established methods include preparing polymers using alkyl halides as transfer agents. This has been studied widely for alkyl iodides through ITP. Alkyl bromides have been explored in literature, and in some cases block copolymers have been prepared. The preparation of polymers using bromoform, has not been extensively studied. Thananukul.*et.al*[1] suggested bromoform acts as a CTA for the polymerisation of acrylamides under UV conditions. However, the mechanism and the synthetic route has yet to be identified. In 1958, Miller[2] suggested bromoform acts as a photoinitiator for the polymerisation of acrylonitriles due to the polarisability of the C-Br bond present in bromoform. Both articles suggested copolymers could be produced due to the presence of labile end groups. Due to this uncertainty, further research was conducted to understand the role of bromoform and produce block copolymers using this method.

6.1.1. Synthesis of PS using bromoform-mediated polymerisation under thermal and UV conditions.

To identify the role of bromoform a series of radical polymerisation experiments were designed. For these experiments, PS was prepared under solution polymerisation to tackle the effect of localised hot spots. THF is a versatile solvent and has been widely used in literature for radical polymerisation of styrene. For each experiment, kinetic studies were conducted by monitoring the progression of molar mass and monomer conversion using GPC and ^{1}H NMR, respectively. Results from the thermal polymerisation of styrene showed the experiments conducted using bromoform in the presence of 0.2 molar equivalents of AIBN, reached high conversion (> 85 %) within 24 hours. The polymers obtained from precipitation had a lower molar mass which were closer to target molar mass and lower dispersity compared to the polymer prepared under using the conventional radical polymerisation.

Results from ^{1}H NMR, FTIR and DSC suggested the successful preparation of PS. The ^{1}H NMR for the precipitated polymers prepared contained broad peaks around 7 ppm and a methylene peak around 1.52 ppm which are both characteristics for PS. FTIR contained vibrations and bands at 700, 1493 and 1600 cm^{-1}, which corresponds to the absorption of monosubstituted benzene. DSC was used to determine the T_g for the polymers produced, for all polymer one transition around 85- 95 °C was observed. These characterisation techniques did not confirm the presence of the labile C-Br end group.

The experiments were then conducted under UV conditions by irradiating the reaction flask with UV light (λ = 100-400 nm) for 6 hours. Due to laboratory working hours, it was difficult to achieve high monomer conversions. The experiments conducted using bromoform in the presence of 0.2 molar equivalents ACPA reached low conversions (< 15 %) after 6 hours. The results showed bromoform does not behave as a photoinitiator for the polymerisation of styrene in THF. This goes against what Miller[2] had suggested for the photopolymerisation of acrylonitriles. Due to the slow propagation rate of styrene, it was difficult to reach high conversion, and as a result it was difficult to understand the role of bromoform under these conditions. For this reason, the experiments were repeated by using MMA, which has a faster propagating rate coefficient compared to styrene.

6.1.2. Synthesis of PMMA using bromoform-mediated polymerisation under thermal and UV conditions

To further investigate the role of bromoform under thermal and UV conditions the experiments were repeated for the polymerisation of MMA. For these experiments 0–2 molar equivalents bromoform was added with 0.2 molar equivalents AIBN. The kinetics of each experiment was studied by taking kinetic samples at different intervals. Results from the thermal polymerisation of MMA in THF, showed all the experiments conducted using bromoform reached high conversion (> 95 %) within 24 hours. The precipitated polymers produced using bromoform had molar masses ranging from 20,000-33,000 g/mol. The polymer produced from the conventional radical polymerisation using 0.2 molar equivalents AIBN had an M_n equal to 58,000 g /mol. This result suggests using bromoform-mediated polymerisation offers some control over the molar mass. The results on the dispersity from using bromoform was not very clear under these conditions.

Further experimentations suggested bromoform can behave as a thermal initiator for the polymerisation of MMA in THF at 70 °C. This was investigated further by using 0.1-1.0 molar equivalents bromoform as a thermal initiator for the polymerisation fo MMA. The results showed using 1.0 molar equivalents of bromoform produced polymers which was closest to the target molar mass. The GPC data for this experiment showed the polymers produced

had an M_n = 9,700 and a $Đ$ = 1.55. Results from Section 4.3.1 also showed that the polymerisation of MMA using bromoform as a thermal initiator was also sensitive to oxygen.

Section 4.3.2. focused on using 1.0 molar equivalents bromoform as a thermal initiator at different reaction temperatures (40-70 °C). The results from this section showed the reaction temperature had a major influence on the observed molar mass, and the conversion reached after 24 hours. The experiments conducted at 60 °C and 70 °C, the conversion after 24 hours was equal to 77 % and 94 %. For the reactions conducted at 50 °C and 40 °C, conversion of 26 % and 22 % was reached after 24 hours. The results showed decreasing the reaction temperature resulted in 'high' molar mass polymers being formed. Using the results obtained from the pseudo first order plot, the apparent rate constant, k_{app} was used to plot an Arrhenius plot to calculate the activation energy. The activation energy for the polymerisation of MMA using 1.0 molar equivalents bromoform as a thermal initiator was calculated to be equal to 95.1 kJ/mol. The results from Section 4.1 and 4.3 suggested bromoform can behave as both a thermal initiator and a transfer agent. From this information, bromoform could be classed as an iniferter, a compound that simultaneously acts as an initiator, a CTA and a terminator. To confirm this, end group analysis should be conducted using techniques such as, MALDi-TOF or elemental analysis

Section 4.4 focused on the preparation of PMMA using bromoform-mediated polymerisation under UV condition. A series of experiments were designed to identify the effect adding bromoform had to the photopolymerisation of MMA. The results showed bromoform does not behave as a photoinitiator for the polymerisation of MMA in THF, which is supported by the results from Section 3.3, for the photopolymerisation of styrene under the same conditions. For these experiments 0.1–2 molar equivalents bromoform was added with 0.2 molar equivalents ACPA. The conversion after 6 hours varied from 51 % when 2 molar equivalents bromoform was added to 69 % when 0.1 molar equivalents are added. The molar mass data showed increasing the quantity of bromoform added resulted in 'low' molar mass polymers being produced. The M_n ranged from 11,000 g/mol to 26,000 g/mol when 2 and 0.1 molar equivalents bromoform was added. The results from these experiments showed that using bromoform offers some control over molar mass compared to conventional radical polymerisation, but under the current experimental conditions, it was difficult to achieve high (> 90 %) conversions.

Section 4.5 included an experiment which monitored the temperature for the duration of the photopolymerisation of MMA for the 6 hours the UV lamp was on. The results from this experiment showed the contents of the reaction flask increased in temperature from 21.5 °C to 40.5 °C within the first hour. After this point, the temperature gradually increases to

42.5 °C for the remainder of the experiment. At this temperature, thermal polymerisation could be taking places which complicates the results. Results from Section 4.3.2 showed bromoform can behave as a thermal initiator at 40 °C and the half-life of ACPA suggests it could behave as a thermal initiator at this temperature.

6.1.3. Synthesis of PMMA-PS block copolymer under thermal conditions

Attempts were made to produce block copolymers using both PS and PMMA produced from the bromoform-mediated polymerisation under thermal conditions. It was discovered the order of homopolymer used as macro-CTA/macro-initiator plays an important role in the final polymer formed. Reactions were first conducted using PS as a macro-initiator/macro-CTA. The results from the ^{1}H NMR and FTIR suggested the successful preparation of PMMA in the final sample. ^{1}H NMR contained signals at 3.55,1.65 and 0.65 ppm which are attributed to the methyl ester, the methylene and methyl group of PMMA. The FTIR spectrum contained stretches resembling the functional groups of PMMA such as; a strong C=O carbonyl stretch at 1730 cm^{-1}, O-CH_3 stretch at 1250 cm^{-1} and C-O bending at 1150 cm^{-1}. The GPC traces for the kinetic samples taken showed no change in retention time for the duration of the reaction, this shows the chain length had not increased. The evidence from ^{1}H NMR, FTIR and the appearance of a shoulder on each GPC traces implies the production of PMMA homopolymer.

Following this, PMMA was used as a macro-initiator and a macro-CTA for the polymerisation of styrene. The results from Section 5.4 showed a linear increase in molar mass for the polymerisation of styrene. The PMMA-*b*-PS prepared had a target ratio of 50:50. The result from ^{1}H NMR showed the actual ratio was 50:170. This result implied a significant amount of styrene monomer had successfully added onto the polymer chain, or PS homopolymer was present in the final product. The results from this experiment suggested the monomer with the slower propagating rate coefficient should be used as the monomer.

DOSY experiments were performed on the block copolymer and the PMMA starting material. The ^{1}H NMR signals corresponding to PMMA and PS were aligned on two different horizontal line indicating different diffusion coefficients. The DOSY spectra suggested the signals for the methyl and methylene group on PMMA had a different diffusion constant compared to the protons on the ester group. This suggested the ester group on PMMA diffused significantly quicker compared to the methylene and methyl group on the same chain. When taking into account the error in each diffusion coefficient the peaks had very similar diffusion coefficient to PS. Therefore, the backbone of the precipitated polymer

contains the segment of PMMA. The DOSY ^{1}H NMR for the PMMA starting material had a significantly larger diffusion coefficient compared to the coefficient of the PMMA protons in the block copolymer. This supports the formation of the block copolymer, due to the ester protons on the new polymer being significantly lower compared to the starting material. The FTIR spectrum for the precipitated polymer contained C-H stretches around 700 cm^{-1} which is characteristic for monosubstituted benzene. The DSC thermogram for the precipitated polymer outlined two T_g at 100 °C, which is characteristic of PS and a high temperature transition at 130 °C which is characteristic of PMMA.

Following this discovery, Section 5.5 focused on preparing block copolymers were prepared with different target degree of. The ratios of PMMA:PS targeted were the following: 10:90, 25:75, 40:60, 60:40, 75:25 and 90:10. The results from these experiments showed using a large quantity of PMMA homopolymer compared to styrene monomer result in a small difference in molar mass. ^{1}H NMR and GPC showed the main product from these reactions were the production of PS homopolymer. The biggest difference observed was when equal amounts of monomer and homopolymer were used. The GPC traces for the precipitated copolymer showed a shorter retention time (larger M_n) is observed for this polymer when a large amount of styrene units is added to a small amount of PMMA.

Section 5.6 focused on the polymerisation of PMMA-*b*-PS using PMMA as a macro-CTA for the polymerisation of styrene using 0.2 molar equivalents of AIBN. The results from the kinetic study showed high conversions being reached after 6 hours but the GPC traces showed no change in retention. The GPC traces showed the appearance of a shoulder on all traces which increased in intensity during the polymerisation. The dispersity for the polymers produced using this technique was much larger compared to using PMMA as a macro-initiator. The final product was collected by precipitation and had a dispersity equal to 4.52. An FTIR for the final polymer showed the presence of benzyl C-H aromatic stretches at 700 cm^{-1}. Using the evidence from the ^{1}H NMR, GPC and FTIR the main product from this reaction was assumed to be PS homopolymer, from the radical polymerisation of styrene using AIBN.

6.2. FUTURE WORK

To identify the role of bromoform in the bromoform-mediated polymerisation, a variety of new experiments should be designed. One factor which should be studied is the influence solvent has on the polymerisation. In this project, THF was used, due to its versatility and being widely used in literature. However, the boiling point of THF is lower than the reaction temperature used, as a result, complications and anomalies could arise due to solvent evaporation. To take this into account, control experiments were set up. To investigate further a series of experiments should be conducted using a wide range of solvents with different quantities of each being used. DMF and toluene have been used in literature for the polymerisation of styrene and MMA and have boiling points above the reaction temperature currently used.[120,121]

The polymerisation of different functional monomers using bromoform-mediated polymerisation would be essential when considering the mechanism involved. Results from Section 4.3.2 showed bromoform can behave as a thermal initiator for the polymerisation of MMA, but not for the polymerisation of styrene (Section 3.2). The experiment using bromoform as a thermal initiator with styrene was repeated 3 times using the same conditions for the polymerisation of MMA. The results from ^{1}H NMR and GPC showed less than 5 % conversion being achieved and no polymer chains being formed after 72 hours for all repeats. This could suggest bromoform can undergo thermolysis and due to the fast propagating rate of MMA, the polymerisation is possible. To confirm this theory more experiments should be conducted using different ester monomers and styrene derivates. It would be useful to polymerise hydrophilic monomers such as acrylamides and hydroxyl functional monomers under the same conditions. If these experiments are successful, this would open the doors to the production of amphiphilic block copolymers.

To investigate the behaviour of bromoform under UV conditions, a new experimental method should be designed. The current apparatus used has limitation to temperature control and irradiation times. Section 4.5 showed that the temperature of the reaction flask increases from 21.5 °C to 42.5 °C after 6 hours irradiation from the UV lamp. At this temperature, some thermal polymerisation can take place, which would complicate results. To tackle this problem the reaction could be conducted at a lower temperature by using an ice bath. For these changes the distance between the UV light and the flask would have to be reconsidered, it may also be difficult to achieve high monomer conversion due to slower polymerisation rates at the lower temperature. For the current apparatus used the UV light could only be used for a maximum of 6 hours, due to the lamp requiring resetting every hour. This could be improved if the source of UV light was from an LED, which excites at a

similar wavelength, and also doesn't release as much as heat compared to the current UV light source. The availability of this light source would have to investigated and the experimental set up would have to be reconsidered.

Due to equipment availability at the university, some parts of the research were not conclusive. For future studies it would be important to characterise the end groups of the polymers prepared using bromoform. This can be achieved by using MALDI-TOF which is a mass spectrometry technique. In this research project FTIR, DSC and NMR were used to evaluate the properties of the final polymer as a result of being prepared in the presence of bromoform. Results from these techniques showed no clear trend or pattern between each polymer. Another important feature would be running DOSY NMR on all the copolymers formed to evaluate if a mixture of polymers had been formed or a block copolymer. Due to limited time constraints and equipment availability, this was not achievable.

One important factor to consider is conducting repeats on all experiments. Each experiment was conducted once due to limited time constraints. However, it would be important to repeat each experiment at least 3 times. The experiments should be conducted in exactly the same procedure and any anomalies present could be identified and removed. The experiments could be repeated without taking any kinetic samples. In some of the experiments, 7 samples were taken by withdrawing 40 μL of the reaction mixture. This mixture would contain bromoform, initiator, monomer and polymer. Taking kinetic samples could result in a significant difference between the observed molar mass obtained from the actual molar mass from bromoform-mediated polymerisation.

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